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(54) Title: AN ULTRALOW DIELECTRIC CONSTANT MATERIAL AS AN INTRALEVEL OR INTERLEVEL DIELECTRIC IN A SEMICONDUCTOR DEVICE, A METHOD FOR FABRICATING THE SAME, AND AN ELECTRONIC DEVICE CONTAINING THE SAME

(57) Abstract: A method for fabricating a thermally stable ultralow dielectric constant film comprising Si, C, O and H atoms in a parallel plate chemical vapor deposition process utilizing plasma enhanced chemical vapor deposition ("PECVD") process is disclosed. Electronic devices containing insulating layers of thermally stable ultralow dielectric constant materials that are prepared by the method are further disclosed. To enable the fabrication of thermally stable ultralow dielectric constant film, specific precursor materials are used, such as, cyclic siloxanes and organic molecules containing ring structures, for instance, tetramethylcycloterasiloxane and cyclopentene oxide. To stabilize plasma in the PECVD reactor and thereby improve uniformity of the deposited film, CO₂ is added to TMCTS as a carrier gas, or CO₂ or a mixture of CO₂ and O₂ are added to the PECVD reactor.

5 AN ULTRALOW DIELECTRIC CONSTANT MATERIAL AS AN
 INTRALEVEL OR INTERLEVEL DIELECTRIC IN A SEMICONDUCTOR
 DEVICE, A METHOD FOR FABRICATING THE SAME, AND AN
 ELECTRONIC DEVICE CONTAINING THE SAME

10 BACKGROUND OF THE INVENTION

Technical Field of the Invention

 The present invention generally relates to a method for fabricating a dielectric material
15 that has an ultralow dielectric constant (or ultralow-k) associated therewith and an
 electronic device containing such a dielectric material. More particularly, the present
 invention relates to a method for fabricating a thermally stable ultralow-k film for use as
 an intralevel or interlevel dielectric in an ultra-large-scale integration ("ULSI") back-end-
 of-the-line ("BEOL") wiring structure and an electronic structure formed by such
20 method.

Description of the Prior Art

 The continuous shrinking in dimensions of electronic devices utilized in ULSI circuits in
 recent years has resulted in increasing the resistance of the BEOL metallization as well as
25 increasing the capacitance of the intralayer and interlayer dielectric. This combined
 effect increases signal delays in ULSI electronic devices. In order to improve the
 switching performance of future ULSI circuits, low dielectric constant (k) insulators and
 particularly those with k significantly lower than silicon oxide are needed to reduce the
 capacitances. Dielectric materials (i.e., dielectrics) that have low-k values have been
30 commercially available. For instance, one such material is polytetrafluoroethylene
 ("PTFE"), which has a k value of 2.0. However, these dielectric materials are not
 thermally stable when exposed to temperatures above 300~350°C. Integration of these
 dielectrics in ULSI chips requires a thermal stability of at least 400°C. Consequently,
 these dielectrics are rendered useless during integration.

- The low-k materials that have been considered for applications in ULSI devices include polymers containing Si, C, O, such as methylsiloxane, methylsilsesquioxanes, and other organic and inorganic polymers. For instance, a paper (N. Hacker *et al.* "Properties of new low dielectric constant spin-on silicon oxide based dielectrics." Mat. Res. Soc. Symp. Proc. 476 (1997): 25) described materials that appear to satisfy the thermal stability requirement, even though some of these materials propagate cracks easily when reaching thicknesses needed for integration in the interconnect structure when films are prepared by a spin-on technique. Furthermore, the precursor materials are high cost and prohibitive for use in mass production. In contrast to this, most of the fabrication steps of very-large-scale-integration ("VLSI") and ULSI chips are carried out by plasma enhanced chemical or physical vapor deposition techniques. The ability to fabricate a low-k material by a plasma enhanced chemical vapor deposition ("PECVD") technique using readily available processing equipment will simplify the material's integration in the manufacturing process, reduce manufacturing cost, and create less hazardous waste.
- A co-pending application (Hydrogenated Oxidized Silicon Carbon Material, U.S. Serial No. 09/107,567, filed on June 19, 1998) assigned to the common assignee of the present invention and incorporated herein by reference in its entirety, described an ultralow dielectric constant material, consisting of Si, C, O and H atoms, having a dielectric constant not more than 3.6, and exhibiting very low crack propagation velocities.
- Another co-pending application (Multiphase Low Dielectric Constant Material and Method of Deposition, U.S. Serial No. 09/320,495, filed on May 16, 1999) assigned to the common assignee of the present invention and incorporated herein by reference in its entirety, described a dual-phase material, consisting of a matrix composed of Si, C, O, and H atoms, a phase composed of mainly C and H atoms, and having a dielectric constant of not more than 3.2. It should be noted that continued reduction of the dielectric constant of such materials will further improve the performance of electronic devices incorporating such dielectrics.
- In view of the foregoing, there is a continued need for developing a dielectric material that has a dielectric constant of not more than about 2.8 and inhibits cracking.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a method for fabricating an ultralow dielectric constant material having a dielectric constant of not more than about 2.8. More preferably, the dielectric constant for the ultralow-k material is in a range of about 1.5 to about 2.5, and most preferably, the dielectric constant is in a range of about 2.0 to about 2.25. It should be noted that all dielectric constants are relative to a vacuum unless otherwise specified.

10 It is another object of the present invention to provide a method for fabricating an ultralow dielectric constant material comprising Si, C, O and H atoms from a mixture of at least two precursors, wherein a first precursor is selected from molecules with ring structures comprising SiCOH components and a second precursor is an organic molecule selected from the group consisting of molecules with ring structures.

15

It is a further object of the present invention to provide a method for fabricating an ultralow dielectric constant film in a parallel plate plasma enhanced chemical vapor deposition ("PECVD") reactor.

20 It is yet a further object of the present invention to provide an improved method for fabricating an ultralow dielectric constant material by depositing a film on a substrate in the presence of CO₂ or CO₂ and O₂, thereby improving uniformity of the deposited film as well as stabilizing the plasma within the PECVD reactor.

25 It is another object of the present invention to provide a method for fabricating an ultralow dielectric constant material for use in electronic structures as an intralevel or interlevel dielectric in a back-end-of-the-line ("BEOL") interconnect structure.

It is yet another object of the present invention to provide a thermally stable ultralow
30 dielectric constant material that has low internal stresses and a dielectric constant of not higher than about 2.8. More preferably, the dielectric constant for the ultralow-k material

is in a range of about 1.5 to about 2.5 and, most preferably, the dielectric constant is in a range of about 2.0 to about 2.25.

It is still another object of the present invention to provide an electronic structure
5 incorporating layers of insulating materials as intralevel or interlevel dielectrics in a back-end-of-the-line ("BEOL") wiring structure in which at least two of the layers of insulating materials comprise an ultralow dielectric constant material of the present invention.

10 It is yet a further object of the present invention to provide an electronic structure, which has layers of the inventive ultralow dielectric constant material as intralevel or interlevel dielectrics in a back-end-of-the-line ("BEOL") wiring structure and which further contains at least one dielectric cap layer as a reactive ion etch ("RIE") mask polish stop or a diffusion barrier.

15 In accordance with the present invention, there is provided a method for fabricating a thermally stable dielectric material that has a matrix comprising Si, C, O, and H atoms and an atomic level nanoporosity. In a preferred embodiment, the dielectric material has a matrix that consists essentially of Si, C, O, and H. The present invention further
20 provides a method for fabricating the dielectric material by reacting a first precursor gas comprising atoms of Si, C, O, and H and at least a second precursor gas comprising atoms of C, H, and optionally O, F and N in a plasma enhanced chemical vapor deposition ("PECVD") reactor. The present invention yet further provides for mixing the first precursor gas with CO₂, or mixing the first and second precursor gases with CO₂ and
25 O₂, thereby stabilizing the plasma in the PECVD reactor and improving the uniformity of the dielectric film deposited on the substrate. The present invention still further provides an electronic structure (i.e., substrate) that has layers of insulating materials as intralevel or interlevel dielectrics used in a back-end-of-the-line ("BEOL") wiring structure, wherein the insulating material can be the ultralow-k film of present invention.

30

In a preferred embodiment, there is provided a method for fabricating a thermally stable ultralow dielectric constant (ultralow-k) film comprising the steps of: providing a plasma enhanced chemical vapor deposition ("PECVD") reactor; positioning an electronic structure (i.e., substrate) in the reactor; flowing a first precursor gas comprising atoms of Si, C, O, and H into the reactor; flowing a second precursor gas mixture comprising atoms of C, H and optionally O, F and N into the reactor; and depositing an ultralow-k film on the substrate. The depositing step may be performed in the presence of CO₂ or CO₂ and O₂. Preferably, the first precursor is selected from molecules with ring structures comprising SiCOH components such as 1, 3, 5, 7-tetramethylcyclotetrasiloxane ("TMCTS" or "C₄H₁₆O₄Si₄"). The second precursor may be an organic molecule selected from the group consisting of molecules with ring structures, preferably with more than one ring present in the molecule. Especially useful, are species containing fused rings, at least one of which contains a heteroatom, preferentially oxygen. Of these species, the most suitable are those that include a ring of a size that imparts significant ring strain, namely rings of 3 or 4 atoms and/or 7 or more atoms. Particularly attractive, are members of a class of compounds known as oxabicyclics, such as cyclopentene oxide ("CPO" or "C₅H₈O").

Optionally, the deposited film of the present invention can be heat treated at a temperature of not less than about 300°C for a time period of at least about 0.25 hour. The method may further comprise the step of providing a parallel plate reactor, which has a conductive area of a substrate chuck between about 300 cm² and about 700 cm², and a gap between the substrate and a top electrode between about 1 cm and about 10 cm. A high frequency RF power is applied to one of the electrodes at a frequency between about 12 MHz and about 15 MHz. Optionally, an additional low frequency power can be applied to one of the electrodes. The heat-treating step may further be conducted at a temperature not higher than about 300°C for a first time period and then at a temperature not lower than about 380°C for a second time period, the second time period being longer than the first time period. The second time period may be at least about 10 times the first time period.

The deposition step for the ultralow dielectric constant film of the present invention may further comprise the steps of: setting the substrate temperature at between about 25°C and about 400°C; setting the high frequency RF power density at between about 0.05 W/cm² and about 2.0 W/cm²; setting the first precursor flow rate at between about 5 sccm and
5 about 1000 sccm; setting the flow rate of the second precursor between about 5 sccm and about 1000 sccm; setting the reactor pressure at a pressure between about 50 mTorr and about 5000 mTorr; and setting the high frequency RF power between about 15 W and about 500 W. Optionally, an ultralow frequency power may be added to the plasma between about 10 W and about 300 W. When the conductive area of the substrate chuck
10 is changed by a factor of X, the RF power applied to the substrate chuck is also changed by a factor of X.

In another preferred embodiment, there is provided a method for fabricating an ultralow-k film comprising the steps of: providing a parallel plate type chemical vapor deposition
15 reactor that has plasma enhancement; positioning a pre-processed wafer on a substrate chuck which has a conductive area of between about 300 cm² and about 700 cm² and maintaining a gap between the wafer and a top electrode between about 1 cm and about 10 cm; flowing a first precursor gas comprising cyclic siloxane molecules into the reactor; flowing at least a second precursor gas comprising organic molecules with ring
20 structures including C, H and O atoms; and depositing an ultralow-k film on the wafer. The depositing step may be performed in presence of CO₂ or CO₂ and O₂. The process may further comprise the step of heat-treating the film after the deposition step at a temperature of not less than about 300°C for at least about 0.25 hour. The process may further comprise the step of applying a RF power to the wafer. The heat-treating step
25 may further be conducted at a temperature of not higher than about 300°C for a first time period and then at a temperature not lower than about 380°C for a second time period, the second time period being longer than the first time period. The second time period may be at least about 10 times the first time period.

30 The cyclic siloxane precursor utilized can be tetramethylcyclotetrasiloxane ("TMCTS") and the organic precursor can be cyclopentene oxide ("CPO"). The deposition step for

the ultralow-k film may further comprise the steps of: setting the wafer temperature at between about 25°C and about 400°C; setting a RF power density at between about 0.05 W/cm² and about 2.0 W/cm²; setting the flow rate of the cyclic siloxane between about 5 sccm and about 1000 sccm; setting the flow rate of the organic precursor between about 5 sccm and about 1000 sccm; and setting the pressure reactor at between about 50 mTorr and about 5000 mTorr. Additionally, the deposition step may further comprise setting a flow ratio of cyclopentene oxide to tetramethylcyclotetrasiloxane to between about 0.1 and about 0.7, preferably between 0.2 and 0.4. The conductive area of the substrate chuck can be changed by a factor X, which leads to a change in RF power by the same factor X.

In still another preferred embodiment, there is provided a method for fabricating a thermally stable ultralow-k dielectric film comprising the steps of: providing a plasma enhanced chemical vapor deposition reactor of a parallel plate type; positioning a wafer on a substrate chuck that has a conductive area between about 300 cm² and about 700 cm² and maintaining a gap between the wafer and a top electrode between about 1 cm and about 10 cm; flowing a precursor gas mixture of a cyclic siloxane with a cyclic organic molecule into the reactor over the wafer, which is kept at a temperature between about room temperature and about 400°C and preferably between about 60°C and about 200°C, at a total flow rate between about 25 sccm and about 500 sccm while keeping the reactor pressure at between about 100 mTorr and about 5000 mTorr; depositing a dielectric film on the wafer under a RF power density between about 0.25 W/cm² and about 0.8 W/cm²; and annealing the ultralow-k film at a temperature of not less than about 300°C for at least about 0.25 hour. The depositing may be performed in the presence of CO₂ or CO₂ and O₂. The inventive method may further comprise the step of annealing the film at a temperature of not higher than about 300°C for a first time period and then at a temperature not lower than about 380°C for a second time period, wherein the second time period is longer than the first time period. The second time period may be set at least about 10 times the first time period. The cyclic siloxane precursor can be tetramethylcyclotetrasiloxane ("TMCTS") and the cyclic organic precursor can be cyclopentene oxide ("CPO").

The present invention is further directed to an electronic structure which has layers of insulating materials as intralevel or interlevel dielectrics in a back-end-of-the-line ("BEOL") interconnect structure which includes a pre-processed semi-conducting substrate that has a first region of metal embedded in a first layer of insulating material, a
5 first region of conductor embedded in a second layer of insulating material of the inventive ultralow-k dielectric, the ultralow-k dielectric comprising Si, C, O and H, and a multiplicity of nanometer-sized pores, and having a dielectric constant of not more than about 2.8, the second layer of insulating material being in intimate contact with the first layer of insulating material, the first region of conductor being in electrical
10 communication with the first region of metal, and a second region of conductor being in electrical communication with the first region of conductor and being embedded in a third layer of insulating material comprising the inventive ultralow-k dielectric, the third layer of insulating material being in intimate contact with the second layer of insulating material. The electronic structure may further comprise a dielectric cap layer situated in-
15 between the second layer of insulating material and the third layer of insulating material. The electronic structure may further comprise a first dielectric cap layer between the second layer of insulating material and the third layer of insulating material, and a second dielectric cap layer on top of the third layer of insulating material.

20 The dielectric cap material can be selected from silicon oxide, silicon nitride, silicon oxynitride, a refractory metal silicon nitride (wherein the refractory metal is selected from the group consisting of Ta, Zr, Hf and W) silicon carbide, carbon doped oxide or SiCOH and their hydrogenated compounds. The first and the second dielectric cap layers may be selected from the same group of dielectric materials. The first layer of insulating
25 material may be silicon oxide or silicon nitride or doped varieties of these materials, such as phosphorus silicate glass ("PSG") or boron phosphorus silicate glass ("BPSG"). The electronic structure may further include a diffusion barrier layer of a dielectric material deposited on at least one of the second and third layers of insulating material. The electronic structure may further comprise a dielectric on top of the second layer of
30 insulating material, which acts as a reactive ion etch ("RIE") hard mask and polish stop layer and a dielectric diffusion barrier layer on top of the dielectric RIE hard mask and

polish stop layer. The electronic structure may further comprise a first dielectric RIE hard mask/polish-stop layer on top of the second layer of insulating material, a first dielectric RIE hard mask/diffusion barrier layer on top of the first dielectric polish-stop layer, a second dielectric RIE hard mask/polish-stop layer on top of the third layer of insulating material, and a second dielectric diffusion barrier layer on top of the second dielectric polish-stop layer. The electronic structure may further comprise a dielectric cap layer of same materials as mentioned above, between an interlevel dielectric of ultralow-k dielectric and an intralevel dielectric of ultralow-k dielectric.

10

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing objects, features and advantages of the present invention will become apparent from the following detailed description and the appended drawings in which:

15 Figure 1 depicts the general electronic structure of a bicyclic ether, also known as a oxabicyclic, which is a preferred compound for the second precursor. In this general schematic, the compound includes two rings, one of which contains an oxygen atom. The size of each ring is determined by the number of repeating methylene groups in each cycle, m and n. In a highly preferred case of cyclopentene oxide, $m = 0$ and $n = 2$.

20

Figure 2 depicts the general electronic structure of an unsaturated bicyclic ether, also known as a unsaturated oxabicyclic, which is a preferred compound for the second precursor. In this general schematic, the compound includes two rings, one of which contains an oxygen atom. The size of each ring is determined by the number of repeating methylene groups in each cycle, l, m and n. The position of the unsaturated bond is determined by m and n. In the example of 9-oxabicyclo[6.1.0]non-4-ene, $l = 0$, $m = 2$ and $n = 2$.

25

Figure 3 depicts a cross-sectional view of a parallel plate chemical vapor deposition reactor according to the present invention.

30

Figure 4 depicts a Fourier Transform Infrared ("FTIR") spectrum obtained from a SiCOH film deposited from a mixture of tetramethylcyclotetrasiloxane ("TMCTS") and He.

Figure 5 depicts a FTIR spectrum obtained from the inventive ultralow-k material deposited from a mixture of TMCTS+He and cyclopentene oxide according to the present invention.

Figure 6 depicts an enlarged, cross-sectional view of an electronic device having an intralevel dielectric layer and an interlevel dielectric layer of ultralow-k material according to the present invention.

Figure 7 depicts an enlarged, cross-sectional view of the electronic structure of Figure 2 having an additional diffusion barrier dielectric cap layer on top of ultralow-k material film according to the present invention.

Figure 8 depicts an enlarged, cross-sectional view of the electronic structure of Figure 3 having an additional RIE hard mask/polish-stop dielectric cap layer and dielectric cap diffusion barrier on top of the polish-stop layer according to the present invention.

Figure 9 depicts an enlarged, cross-sectional view of the electronic structure of Figure 4 having additional RIE hard mask/polish-stop dielectric layers on top of the interlevel ultralow-k material film according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

The present invention discloses a method for fabricating a thermally stable ultralow dielectric constant film in a parallel plate plasma enhanced chemical vapor deposition ("PECVD") reactor. The material disclosed in the preferred embodiment contains a matrix of a hydrogenated oxidized silicon carbon material (SiCOH) comprising Si, C, O and H in a covalently bonded network and having a dielectric constant of not more than about 2.8, which may further contain molecular scale voids, approximately 0.5 to 20

nanometer in diameter, further reducing the dielectric constant to values below about 2.0. More preferably, the dielectric constant for the ultralow-k film is in a range of about 1.5 to about 2.5, and most preferably the dielectric constant is in a range of about 2.0 to about 2.25. To produce an ultralow-k thermally stable film, a specific geometry of the deposition reactor with specific growth conditions is necessary. For instance, in the parallel plate reactor, a conductive area of the substrate chuck should be between about 300 cm² and about 700 cm², with a gap between the substrate and a top electrode between about 1 cm and about 10 cm. A RF power is applied to the substrate. In accordance with the present invention, the ultralow dielectric constant film is formed from a mixture of a cyclic siloxane precursor such as TMCTS and a second precursor, which is an organic molecule, selected from the group consisting of molecules with ring structures, such as cyclopentene oxide, in a specifically configured reaction reactor under specific reaction conditions. In accordance with another embodiment of the present invention, the ultralow dielectric constant film may be formed in presence of CO₂ or CO₂ and O₂. The low dielectric constant film of the present invention can further be heat treated at a temperature not less than about 300°C for at least about 0.25 hour to reduce the dielectric constant. During this heat treatment step, molecule fragments derived from the second precursor gas (or gas mixture) comprising carbon and hydrogen and optionally oxygen atoms may thermally decompose and may be converted into smaller molecules which are released from the film. Optionally, further development of voids may occur in the film by the process of conversion and release of the molecule fragments. The film density is thus decreased.

The present invention provides a method for preparing a material that has an ultralow dielectric constant, i.e., lower than about 2.8, which is suitable for integration in a BEOL wiring structure. More preferably, the dielectric constant for the inventive ultralow-k film is in a range of about 1.5 to about 2.5 and, most preferably, the dielectric constant is in a range of about 2.0 to about 2.25. The inventive films can be prepared by choosing at least two suitable precursors and a specific combination of processing parameters as described herein below. Preferably, the first precursor is selected from molecules with ring structures comprising SiCOH components such as 1,3,5,7-

tetramethylcyclotetrasiloxane (TMCTS or $C_4H_{16}O_4Si_4$) or octamethylcyclotetrasiloxane (OMCTS or $C_8H_{24}O_4Si_4$). More generally, the first precursor is of a class of cyclic alkylsiloxanes comprising a ring structure including an equivalent number of Si and O atoms bonded in an alternating fashion to which alkyl groups (such as methyl, ethyl, propyl or higher or branched analogs as well as cyclic hydrocarbons such as cyclopropyl, cyclopentyl, cyclohexyl, and higher analogs) are covalently bonded to at least one of the silicon atoms, including the cases where all the silicon atoms have two alkyl groups attached. Such alkyl groups may be similar or dissimilar. Additionally, the silicon atoms of such cyclic siloxanes may be bonded to hydrogen, in which case these compounds may be considered partially alkylated hydrosiloxanes.

The second precursor may be chosen from organic molecules, containing C, H, and O atoms and containing at least one ring, that have suitable volatility such that they may be introduced to the deposition reactor as a vapor by manipulation of temperature and pressure. Additionally, other atoms such as N, S, Si, or halogens may be contained in the precursor molecule. Additionally, more than one ring may be present in the precursor molecule. Especially useful, are species containing fused rings, at least one of which contains a heteroatom, preferentially oxygen. Of these species, the most suitable are those that include a ring of a size that imparts significant ring strain, namely rings of 3 or 4 atoms and/or 7 or more atoms. Particularly attractive, are members of a class of compounds known as oxabicyclics. Among the readily available examples of these, are 6-oxabicyclo[3.1.0]hexane or cyclopentene oxide (bp = 102°C at 760 mm Hg); 7-oxabicyclo[4.1.0]heptane or cyclohexene oxide (bp = 129°C at 760 mm Hg); 9-oxabicyclo[6.1.0]nonane or cyclooctene oxide (bp = 55°C at 5 mm Hg); and 7-oxabicyclo[2.2.1]heptane or 1,4-epoxycyclohexane (bp = 119°C at 713 mm Hg). More generally, species that fit the formula shown in Figure 1 may be considered suitable.

Additionally, the second precursor may have some degree of unsaturation as in 9-oxabicyclo[6.1.0]non-4-ene (bp = 195°C at 760 mm Hg) or compounds of the general structure shown in Figure 2. Furthermore, the second precursor may have additional functionalities including, but not limited to: ketones, aldehydes, amines, amides; imides,

ethers, esters, anhydrides, carbonates, thiols, thioethers and the like, as in

7-oxabicyclo[4.1.0]heptan-2-one (bp = 77°C at 15 mmHg) and

3-oxabicyclo[3.1.0]hexane-2,4-dione (bp = 100°C at 5 mmHg).

Furthermore, the first precursor may further be mixed with CO₂ as a carrier gas or the
5 first and second precursor gases may be mixed with CO₂ or a mixture of CO₂ and O₂ in
the PECVD reactor. The addition of CO₂ to the first precursor as a carrier gas, or the
addition of CO₂ or a mixture of CO₂ and O₂ to the first and second precursors in the
PECVD reactor provides a stabilizing effect on plasma in the PECVD reactor and
improves the uniformity of the film deposited on the substrate. When CO₂ is admixed
10 with the first and second precursors, the amount of CO₂ may be from about 25 sccm to
about 1000 sccm, and more preferably from about 50 sccm to about 500 sccm. When a
mixture of CO₂ and O₂ is admixed with the first and second precursors, the amount of
CO₂ admixed may be from about 25 sccm to about 1000 sccm and the amount of O₂
admixed may be from about 0.5 sccm to 50 sccm. More preferably, the amount of CO₂ is
15 from about 50 sccm to about 500 sccm and the amount of O₂ is from about 1 sccm to
about 30 sccm.

As shown in Figure 3, parallel plate plasma enhanced chemical vapor deposition
("PECVD") reactor 10 is the type used for processing 200 mm wafers. The inner
20 diameter, X, of the reactor 10 is approximately 13 inches, while its height, Y, is
approximately 8.5 inches. The diameter of substrate chuck 12 is approximately 10.8
inches. Reactant gases are introduced into reactor 10 through a gas distribution plate
("GDP") 16 that is spaced apart from substrate chuck 12 by a gap Z of about 1 inch, and
are exhausted out of reactor 10 through a 3-inch exhaust port 18. RF power 20 is
25 connected to GDP 16, which is electrically insulated from reactor 10, and substrate chuck
12 is grounded. For practical purposes, all other parts of the reactor are grounded. In a
different embodiment, RF power 20 can be connected to substrate chuck 12 and
transmitted to substrate 22. In this case, the substrate acquires a negative bias, whose
value is dependent on the reactor geometry and plasma parameters. In another
30 embodiment, more than one electrical power supply can be used. For instance, two
power supplies can operate at the same RF frequency, or one may operate at a low

frequency and one at a high frequency. The two power supplies may be connected both to the same electrode or to separate electrodes. In another embodiment, the RF power supply can be pulsed on and off during deposition. Process variables controlled during deposition of the low-k films are RF power, precursor mixture and flow rate, pressure in reactor, and substrate temperature.

Surfaces 24 of reactor 10 may be coated with an insulating coating material. For instance, one specific type of coating is applied on reactor walls 24 to a thickness of several mils. Another type of coating material that may be used on substrate chuck 12 is a thin coating of alumina or other insulator resistant to etching with an oxygen plasma.

10 The temperature of the heated wafer chuck controls the substrate temperature.

In accordance the present invention, suitable first and second precursors and specific combination of processing parameters described herein above are employed such that the inventive ultralow-k material prepared preferably comprises: between about 5 and about 40 atomic percent of Si; between about 5 and about 45 atomic percent of C; between 0 and about 50 atomic percent of O; and between about 10 and about 55 atomic percent of H.

The main process variables controlled during a deposition process for a film are the RF power, the flow rates of the precursors, flow rate of CO₂, or flow rates of CO₂ and O₂, the reactor pressure and the substrate temperature. Provided herein below are several examples of deposition of films utilizing a first precursor tetramethylcyclotetrasiloxane (TMCTS) and a second precursor cyclopentene oxide ("CPO"), as well as deposition of films in presence of CO₂ or CO₂ and O₂, according to the present invention. In the examples 1-2, the TMCTS precursor vapors were transported into the reactor by using He as a carrier gas, while in the examples 3, the TMCTS was transported by a liquid delivery system. In the examples 5-7, the TMCTS precursor vapors were transported into the reactor using CO₂ as a carrier gas, while in the example 8, the TMCTS was transported by a liquid delivery system. Optionally, the films were heat treated at 400°C after deposition to reduce k.

- It should be emphasized that the fabrication method according to the present invention is only possible by utilizing a deposition reactor that has a specific geometry with uniquely defined growth conditions. When a reactor of different geometry is used under the defined growth conditions, the films produced may not achieve the ultralow dielectric constant. For instance, the parallel plate reactor according to the present invention should have an area of the substrate chuck of between about 300 cm² and about 700 cm², and preferably between about 500 cm² and about 600 cm². The gap between the substrate and the gas distribution plate (or top electrode) is between about 1 cm and about 10 cm, and preferably between about 1.5 cm and about 7 cm. A RF power is applied to one of the electrodes at a frequency between about 12 MHz and about 15 MHz, and preferably at about 13.56 MHz. A low frequency, below 1 MHz, power can optionally be applied at the same electrode as the RF power, or to the opposite electrode at a power density of 0 to 0.3 W/cm².
- The deposition conditions utilized are also critical to enable a successful implementation of the deposition process according to the present invention. For instance, a wafer temperature of between about 25°C and about 325°C, and preferably of between about 60°C and about 200°C is utilized. A RF power density between about 0.05 W/cm² and about 1.0 W/cm², and preferably between about 0.25 W/cm² and about 0.8 W/cm² is utilized. A reactant gas flow rate of TMCTS between about 5 sccm and about 1000 sccm, and preferably between about 25 sccm and about 200 sccm is utilized. A reactant gas flow rate of CPO between about 5 sccm and about 1000 sccm, and preferably between about 10 sccm and about 120 sccm is utilized. A total reactant gas flow rate of TMCTS-CO₂, where CO₂ is used as a carrier gas is from about 25 sccm to about 1000 sccm, flow rates for CO₂ and O₂ mixture are respectively from about 25 sccm to 1000 sccm for CO₂ and from about 0.5 sccm to about 50 sccm for O₂, and flow rate for CO₂ from about 15 sccm to about 1000 sccm. A total reactant gas flow rate of TMCTS-CO₂, where CO₂ is used as a carrier gas is preferably from about 50 sccm to 500 sccm, flow rates for CO₂ and O₂ mixture are preferably respectively from about 50 sccm to about 500 sccm for CO₂ and from about 1 sccm to about 30 sccm for O₂, and flow rate for CO₂ preferably is from about 50 sccm to about 500 sccm. Reactor pressure during the

deposition process between about 50 mTorr and about 5000 mTorr, and preferably between about 100 mTorr and about 3000 mTorr is utilized.

- It should be noted that a change in the area of the substrate chuck by a factor, X, i.e., a change from a value in the range between about 300 cm² and about 700 cm², will change the RF power by a factor, X, from that previously specified. Similarly, a change in the area of the substrate chuck by a factor, Y, and a change in the gap between the gas distribution plate and the substrate chuck by a factor, Z, from that previously specified, will be associated with a change by a factor, YZ, in the gas flow rates from that previously specified. If a multistation deposition reactor is used, the area of the substrate refers to each individual substrate chuck and the flow rates of the gases refer to one individual deposition station. Accordingly, total flow rates and total power input to the reactor are multiplied by a total number of deposition stations inside the reactor.
- 15 The deposited films are stabilized before undergoing further integration processing. The stabilization process can be performed in a furnace-annealing step at about 300°C to about 400°C for a time period between about 0.5 hours and about 4 hours. The stabilization process can also be performed in a rapid thermal annealing process at temperatures above about 300°C. The dielectric constants of the films obtained according to the present invention are lower than about 2.8. The thermal stability of the films obtained according to the present invention in non-oxidizing ambient is up to at least a temperature of about 400°C.

- The electronic devices formed according to the present invention are shown in Figures 6-9. It should be noted that the devices shown in Figures 6-9, are merely illustrated as examples according to the present invention, while countless other devices can also be formed according to the present invention.

- Figure 6 depicts electronic device 30 that is built on a silicon substrate 32. On top of silicon substrate 32, insulating material layer 34 is formed with a first region of metal 36 embedded therein. After a chemical mechanical polishing ("CMP") process is conducted

on first region of metal 36, a film such as an ultralow-k film 38 is deposited on top of first layer of insulating material 34 and first region of metal 36. First layer of insulating material 34 may be suitably formed of silicon oxide, silicon nitride, doped varieties of these materials, or any other suitable insulating materials. Ultralow-k film 38 is patterned
5 by a photolithography process and conductor layer 40 is deposited therein. After a CMP process on first conductor layer 40 is carried out, second layer of ultralow-k film 44 is deposited by a plasma enhanced chemical vapor deposition ("PECVD") process overlying first ultralow-k film 38 and first conductor layer 40. Conductor layer 40 may be deposited of a metallic conductive material or a non-metallic conductive material. For
10 instance, a metallic conductive material of aluminum or copper, or a non-metallic material such as nitride or polysilicon may be utilized. First conductor 40 is in electrical communication with first region of metal 36.

A second region of conductor 50 is formed, after a photolithographic process in second
15 ultralow-k film layer 44 is conducted, followed by a deposition process for the second conductor material. Second conductor 50 may also be deposited of either a metallic material or a non-metallic material, similar to that used in depositing the first conductor layer 40. The second region of conductor 50 is in electrical communication with the first region of conductor 40 and is embedded in the second layer of ultralow-k insulator 44.
20 The second layer of ultralow-k film is in intimate contact with the first layer of insulating material 38. In this specific example, the first layer of insulating material 38, which is an ultralow-k material according to the present invention, serves as an intralevel dielectric material, while the second layer of insulating material, i.e., the ultralow-k film 44, serves as both an intralevel and an interlevel dielectric. Based on the low dielectric constant of
25 the ultralow-k film, superior insulating property can be achieved by first insulating layer 38 and second insulating layer 44.

Figure 7 depicts electronic device 60 according to the present invention, similar to that of electronic device 30 shown in Figure 6, but with additional dielectric cap layer 62
30 deposited between first insulating material layer 38 and second insulating material layer 44. Dielectric cap layer 62 can be suitably formed of a material such as silicon oxide,

silicon nitride, silicon oxynitride, silicon carbide, silicon carbo-oxide (SiCO), modified ultralow-k and their hydrogenated compounds, as well as refractory metal silicon nitride, wherein the refractory metal is selected the group consisting of: Ta, Zr, Hf, and W.

Additional dielectric cap layer 62 functions as a diffusion barrier layer for preventing
5 diffusion of first conductor layer 40 into second insulating material layer 44 or into the
lower layers, especially into layers 34 and 32.

Figure 8 depicts another alternate embodiment of electronic device 70 according to the present invention. In electronic device 70, two additional dielectric cap layers 72 and 74
10 that act as an RIE mask and CMP (chemical-mechanical polishing) polish stop layer are used. First dielectric cap layer 72 is deposited on top of first insulating material layer 38. The function of dielectric layer 72 is to provide an end point for the CMP process utilized in planarizing first conductor layer 40. Polish stop layer 72 can be deposited of a suitable dielectric material such as silicon oxide, silicon nitride, silicon oxynitride, silicon carbide,
15 silicon carbo-oxide (SiCO), modified ultralow-k and their hydrogenated compounds, as well as refractory metal silicon nitride, wherein the refractory metal is selected from the group consisting of: Ta, Zr, Hf and W. The top surface of dielectric layer 72 is at the same level as first conductor layer 40. A second dielectric layer 74 can be added on top of second insulating material layer 44 for the same purposes.

20

Figure 9 depicts still another alternate embodiment of electronic device 80 according to the present invention. In this alternate embodiment, an additional layer of dielectric 82 is deposited and thus divides second insulating material layer 44 into two separate layers 84 and 86. Intralevel and interlevel dielectric layer 44, as depicted in Figure 8, is therefore
25 divided into interlayer dielectric layer 84 and intralevel dielectric layer 86 at the boundary between interconnect 92 and interconnect 94, as depicted in Figure 9. An additional diffusion barrier layer 96 is further deposited on top of the upper dielectric layer 74. The additional benefits provided by this alternate embodiment of the electronic structure 80 is that the dielectric layer 82 acts as a RIE etch stop providing superior
30 interconnect depth control.

The following examples are presented to illustrate the fabrication of the ultralow-k dielectric film in accordance with the present invention as well as to demonstrate advantages that can be obtained therefrom:

5 **Example 1**

In this example, according to Figure 3, a wafer is first prepared by introducing the wafer into reactor 10 through a slit valve 14 and pre-etching the wafer by argon gas. In this wafer preparation process, the wafer temperature is set at about 180°C and the argon flow rate is set at about 25 sccm, to achieve a pressure of about 100 mTorr. A RF power is then turned on to about 125 W for about 60 seconds. The RF power and the argon gas flow are then turned off.

The TMCTS precursor is carried into the reactor reactor using He as a carrier gas; He is at a pressure of about 5 psig at the inlet to the TMCTS container. The ultralow-k film according to the present invention can be deposited by first establishing gas flows of TMCTS+He and CPO to desired flow rates and pressure, i.e., at about 20 sccm of TMCTS+He and about 6 sccm of CPO and about 100 mTorr. A RF power is then turned on at about 15 W for a time period of about 50 minutes. The RF power and the gas flow are then turned off. The wafer is then removed from reaction reactor 10.

20 To reduce the dielectric constant of the deposited films and to further improve their thermal stability, i.e., to make them stable at temperatures greater than 300°C, the films are post annealed to evaporate the volatile contents and to dimensionally stabilize the films. The post annealing process can be carried out in an annealing furnace by the following steps. The furnace is first purged for about 5 minutes (with the film samples in a load station) with nitrogen at a flow rate of about 10 liters/minute. The film samples are then transferred into the furnace reactor to start the post annealing cycle of heating the films to about 280°C at a heating rate of about 5°C/minute, holding at about 280°C for about 5 minutes, heating at a second heating rate of about 5°C/minute to about 400°C, 30 holding at about 400°C for about 4 hours, turning the furnace off and allowing the film samples to cool to a temperature of below about 100°C. A suitable first holding

temperature may be between about 280°C and about 300°C, while a suitable second holding temperature may be between about 300°C and about 400°C.

Results of the first embodiment are now discussed in reference to Figures 4 and 5. Figure 4 presents a Fourier transform infrared ("FTIR") spectrum of a typical SiCOH film. The spectrum displays a strong Si-O absorption band at about 1000-1100 cm^{-1} , a Si-CH₃ absorption peak at about 1275 cm^{-1} , a Si-H absorption band at about 2150-2250 cm^{-1} and small C-H absorption peaks at about 2900-3000 cm^{-1} . The relative intensities of the CH, SiH and SiCH₃ peaks as compared to the SiO peak of the SiCOH film are presented in Table 1 herein below.

Figure 5 presents the FTIR spectrum obtained from an ultralow-k film prepared from a mixture of (TMCTS+He)+CPO in accordance with the present invention. The spectrum displays the Si-O, Si-CH₃, and C-H absorption peaks, as in Figure 4. However, the Si-H peak is missing the intensity of the C-H absorption band at about 2900-3000 cm^{-1} is much stronger for the ultralow-k film than for the SiCOH film shown in Figure 4. The relative intensities of the CH, and SiCH₃ peaks as compared to the SiO peak for this film are also shown in Table 1. As particularly illustrated in Table 1, the integrated area of C-H peak of the ultralow-k film is 40% of the Si-CH₃ peak, while it is only 2% of the Si-CH₃ peak in the SiCOH film. This is a clear indication that the ultralow-k film contains a significant amount of a secondary CH_x (hydrocarbon) phase in addition to the SiCOH phase. Another characteristic of the FTIR spectrum of the ultralow-k film is the splitting of the Si-O peak into two peaks at about 1139 cm^{-1} and about 1056 cm^{-1} , as particularly illustrated in Figure 5.

Table 1. Relative integrated intensities of FTIR absorption peak

MATERIAL	CH/SiO (%)	SiH/SiO (%)	SiCH/SiO (%)
SiCOH	2	7	5
Ultralow-k	10	0	4

Example 2

In this example, a wafer is prepared as described in Example 1, but the wafer temperature is set at about 300°C. The TMCTS precursor is then carried into the reactor using He as a carrier gas; He is at a pressure of about 5 psig at the inlet to the TMCTS container. The
5 ultralow-k film according to the present invention can be deposited by first establishing gas flows of TMCTS+He and CPO to desired flow rates and pressure, i.e., at about 150 sccm of TMCTS+He and about 50 sccm of CPO and about 2000 mTorr. A RF power is then turned on at about 150 W for a time period of about 10 minutes. The RF power and the gas flow are then turned off. The wafer is then removed from the reaction reactor
10 and annealed as described in Example 1.

Example 3

In this example, a reactor containing 6 deposition stations is used. The temperature of the wafer chuck is set at about 350°C. The TMCTS precursor is carried into the reactor
15 using a liquid delivery system at a flow rate of at about 5 ml/min and the CPO is flown at a rate of about 900 sccm and the pressure is stabilized at about 3000 mTorr. A total RF power of about 600 W and a low frequency power of about 300 W are applied to the reactor. The ultralow-k film deposition is performed on the wafer at each station with the wafer moving to the next station after a preset time interval. The wafer is removed from
20 the reaction reactor after passing the last deposition station, and annealed as described in Example 1.

In the foregoing examples, the plasma was operated in a continuous mode. In Example 4
25 herein below, the plasma is operated in a pulsed mode.

Example 4

In this example, the deposition is performed under conditions similar to Example 1, but the plasma is operated in a pulsed mode, i.e., with a duty cycle of about 50% and a plasma-on time of about 50 msec to about 100 msec. After removal of the wafer from
30 reactor 10, the wafer with the deposited film is annealed as described in Example 1.

As described in the foregoing examples, the films that are prepared have dielectric constants in the range of about 2.0 to about 2.25.

Example 5

- 5 In this example, according to Figure 3, a wafer is first prepared by introducing the wafer into reactor 10 through a slit valve 14 and pre-etching the wafer by argon gas. In this wafer preparation process, the wafer temperature is set at about 180°C and the argon flow rate is set at about 25 sccm, to achieve a pressure of about 100 mTorr. A RF power is then turned on to about 125 W for about 60 seconds. The RF power and the argon gas
10 flow are then turned off.

- The TMCTS precursor is carried into the reactor reactor using CO₂ as a carrier gas; CO₂ is at a pressure of about 5 psig at the inlet to the TMCTS container. The ultralow-k film according to the present invention can be deposited by first establishing gas flows of
15 TMCTS+ CO₂ and CPO to desired flow rates and pressure, i.e., at about 20 sccm of TMCTS+ CO₂ and about 10 sccm of CPO and about 100 mTorr. A RF power is then turned on at about 15 W for a time period of about 50 minutes. The RF power and the gas flow are then turned off. The wafer is then removed from reaction reactor 10.
- 20 To reduce the dielectric constant of the deposited films and to further improve their thermal stability, i.e., to make them stable at temperatures greater than 300°C, the films are post annealed to evaporate the volatile contents and to dimensionally stabilize the films. The post annealing process can be carried out in an annealing furnace by the following steps. The furnace is first purged for about 5 minutes (with the film samples in
25 a load station) with nitrogen at a flow rate of about 10 liters/minute. The film samples are then transferred into the furnace reactor to start the post annealing cycle of heating the films to about 280°C at a heating rate of about 5°C/minute, holding at about 280°C for about 5 minutes, heating at a second heating rate of about 5°C/minute to about 400°C, holding at about 400°C for about 4 hours, turning the furnace off and allowing the film
30 samples to cool to a temperature of below about 100°C. A suitable first holding

temperature may be between about 280°C and about 300°C, while a suitable second holding temperature may be between about 300°C and about 400°C.

Example 6

- 5 In this example, a wafer is prepared as described in Example 5, but the wafer temperature is set at about 300°C. The TMCTS precursor is then carried into the reactor using CO₂ as a carrier gas; CO₂ is at a pressure of about 5 psig at the inlet to the TMCTS container. The ultralow-k film according to the present invention can be deposited by first establishing gas flows of TMCTS+ CO₂ and CPO to desired flow rates and pressure, i.e.,
10 at about 150 sccm of TMCTS+ CO₂ and about 75 sccm of CPO and about 2000 mTorr. A RF power is then turned on at about 150 W for a time period of about 10 minutes. The RF power and the gas flow are then turned off. The wafer is then removed from the reaction reactor 10 and annealed as described in Example 5.
- 15 In the foregoing examples, the plasma was operated in a continuous mode. In Example 3 herein below, the plasma is operated in a pulsed mode.

Example 7

- 20 In this example, the deposition is performed under conditions similar to Example 5, but the plasma is operated in a pulsed mode, i.e., with a duty cycle of about 50% and a plasma-on time of about 50 msec to about 100 msec. After removal of the wafer from reactor 10, the wafer with the deposited film is annealed as described in Example 5.

Example 8

- 25 In this example, a reactor including 6 deposition stations is used. The temperature of the wafer chuck is set at about 350°C. The TMCTS precursor is carried into the reactor using a liquid delivery system at a flow rate of about 5 ml/min, the CPO being flown at a rate of about 250 sccm and the pressure being stabilized at about 4000 mTorr. The CO₂ at a flow rate of about 5000 sccm and O₂ at a flow rate of about 250 sccm are admixed
30 with the gas mixture of TMCTS and CPO in the reactor. The addition of the CO₂ and O₂ mixture stabilizes the plasma and improves the film uniformity. A total high frequency

RF power of about 600 W and a low frequency RF power of about 300 W are applied to the reactor. The ultralow-k film deposition is performed on the wafer at each station with the wafer moving to the next station after a preset time interval. The wafer is removed from the reactor after passing the last deposition station, and the wafer may further be
5 optionally annealed as particularly described in Example 5 hereinabove.

A rapid thermal annealing ("RTA") process may also be used to stabilize ultralow-k films. The films obtained according to the present invention, are characterized by dielectric constants k less than about 2.8, and are thermally stable for integration in a
10 back-end-of-the-line ("BEOL") interconnect structure, which is normally processed at temperatures of up to about 400°C. The teachings of the present invention can therefore be easily adapted in producing films as intralevel and interlevel dielectrics in back-end-of-the-line processes for logic and memory devices.

15 The method and electronic structures formed according to the present invention have therefore been thoroughly demonstrated in the above descriptions and in the appended drawings of Figures 1-9. It should be emphasized that the examples of the electronic structures shown in Figures 6-9 are merely used to illustrate the inventive method that can be applied in the fabrication of countless electronic devices.

20

While the present invention has been described in an illustrative manner, it should be understood that the terminology used is intended to be in a nature of words of description rather than of limitation.

25 Furthermore, while the present invention has been particularly shown and described with respect to a preferred embodiment and several alternate embodiments, it is to be appreciated that those skilled in the art may readily apply these teachings to other possible variations of the present invention without departing from the spirit and scope of the present invention.

30

CLAIMS

- 1 1. A method for fabricating a thermally stable ultralow dielectric constant
2 film comprising the steps of:
3 providing a plasma enhanced chemical vapor deposition (PECVD) reactor;
4 positioning a substrate in said PECVD reactor;
5 flowing a first precursor gas comprising cyclic siloxane molecules into
6 said PECVD reactor;
7 flowing at least a second precursor gas comprising organic molecules with
8 ring structures having C, H and O atoms into said PECVD reactor; and
9 depositing a film comprising Si, C, O and H and a multiplicity of
10 nanometer-sized pores on said substrate.
- 1 2. The method according to Claim 1, further comprising the step of:
2 mixing said first precursor gas with an inert carrier gas.
- 1 3. The method according to Claim 1, wherein said PECVD reactor is of a
2 parallel plate type reactor.
- 1 4. The method according to Claim 1, wherein said film is optionally
2 heated after deposition at a temperature not less than about 300°C for at least about 0.25
3 hours.
- 1 5. The method according to Claim 1, wherein said film has a dielectric
2 constant of not more than about 2.8.
- 1 6. The method according to Claim 1, wherein said film has a dielectric
2 constant of not more than about 2.3.
- 1 7. The method according to Claim 1, wherein said film has a dielectric
2 constant in a range from about 1.5 to about 2.5.

1 8. The method according to Claim 1, wherein said film comprises:
2 between about 5 and about 40 atomic percent of Si;
3 between about 5 and about 45 atomic percent of C;
4 between 0 and about 50 atomic percent of O; and
5 between about 10 and about 55 atomic percent of H.

1 9. The method according to Claim 1, further comprising the step of:
2 providing a parallel plate reactor having an area of a substrate chuck
3 between about 300 cm² and about 700 cm², and a gap between the substrate and a top
4 electrode between about 1 cm and about 10 cm.

1 10. The method for fabricating a thermally stable ultralow dielectric
2 constant film according to Claim 3, said method further comprising the step of:
3 applying a RF power to an electrode of said parallel plate PECVD reactor.

1 11. The method according to Claim 1, further comprising a step of:
2 heat treating said film at a temperature not higher than about 300°C for a
3 first time period and heat treating said film at a temperature not lower than about 300°C
4 for a second time period, said second time period being longer than said first time period.

1 12. The method according to Claim 11, wherein said second time period is
2 at least about ten times that of said first time period.

1 13. The method according to Claim 1, wherein said cyclic siloxane is
2 selected from the group consisting of: tetramethylcyclotetrasiloxane and
3 octamethylcyclotetrasiloxane.

1 14. The method according to Claim 1, wherein said cyclic siloxane is
2 tetramethylcyclotetrasiloxane.

1 15. The method according to Claim 1, wherein said organic molecules
2 comprise species of fused rings including ring structures that impart significant ring
3 strain, wherein said ring structures that impart significant ring strain include rings of 3, 4,
4 7 or more atoms.

1 16. The method according to Claim 1, wherein said organic molecules are
2 cyclopentene oxide.

1 17. The method according to Claim 1, wherein said step of depositing the
2 film further comprises the steps of:
3 setting a temperature for said substrate at between about 25°C and about
4 400°C; and
5 setting a RF power density at between about 0.05 W/cm² and about 2.0
6 W/cm².

1 18. The method according to Claim 1, wherein said step of depositing the
2 film further comprises:
3 setting flow rates for said cyclic siloxane at between about 5 sccm and
4 about 1000 sccm.

1 19. The method according to Claim 18, wherein said flow rates for said
2 cyclic siloxane are at between about 25 sccm and about 200 sccm.

1 20. The method according to Claim 1, wherein said step of depositing said
2 film further comprises:
3 setting flow rates said for said organic molecules at between about 5 sccm
4 and about 1000 sccm.

1 21. The method Claim 20, wherein said flow rates for said organic
2 molecules are at between about 25 sccm and about 200 sccm.

1 22. The method according to Claim 1, wherein said step of depositing said
2 film further comprises:
3 setting a pressure for said PECVD reactor at between about 50 mTorr and
4 about 5000 mTorr.

1 23. The method according to Claim 22, wherein said pressure for said
2 PECVD reactor is between about 100 mTorr and about 3000 mTorr.

1 24. The method according to Claim 1, wherein said step of depositing said
2 film further comprises:
3 setting a flow rate ratio of organic molecules of cyclopentene oxide to
4 cyclic siloxane of tetramethylcyclotetrasiloxane to between about 0.1 and about 0.7.

1 25. The method for fabricating a thermally stable ultralow dielectric
2 constant film according to Claim 24, wherein said flow rate ratio of said cyclopentene
3 oxide to said tetramethylcyclotetrasiloxane is between about 0.2 and about 0.4.

1 26. The method according to Claim 1, said method further comprising:
2 providing a parallel plate plasma enhanced chemical vapor deposition
3 chamber.

1 27. The method according to Claim 1, wherein plasma in said PECVD
2 reactor is run in a continuous mode.

1 28. The method according to Claim 1, wherein plasma in said PECVD
2 reactor is run in a pulsed mode.

1 29. The method according to Claim 9, wherein a change in the area of said
2 substrate chuck by a factor, X, changes the RF power by a factor, X.

1 30. The method according to Claim 9, wherein a change in the area of the
2 substrate chuck by a factor, Y, and a change in the gap between a gas distribution plate
3 and the substrate chuck by a factor, Z, changes gas flow rates by a factor, YZ, such that
4 residence time in plasma is maintained.

1 31. The method according to claim 18, wherein when said PECVD reactor
2 includes a plurality of depositions stations then the flow rates of said cyclic siloxane are
3 multiplied by a total number of deposition stations in said PECVD reactor.

1 32. A method for fabricating a thermally stable ultralow-k film comprising
2 the steps of:
3 providing parallel plate type plasma enhanced chemical vapor deposition
4 (PECVD) reactor;
5 positioning a pre-processed wafer on a substrate chuck having an area
6 between about 300 cm² and about 700 cm² and maintaining a gap between said wafer and
7 a top electrode between about 1 cm and about 10 cm;
8 flowing a first precursor gas comprising cyclic siloxane molecules into
9 said PECVD reactor;
10 flowing at least a second precursor gas comprising organic molecules with
11 ring structures having C, H and O atoms; and
12 depositing an ultralow-k film on said wafer.

1 33. A method for fabricating a thermally stable ultralow-k film comprising
2 the steps of:
3 providing a parallel plate type plasma enhanced chemical vapor deposition
4 (PECVD) reactor;
5 positioning a wafer on a substrate chuck having an area between about 300
6 cm² and about 700 cm², and maintaining a gap between the wafer and a top electrode
7 between about 1 cm and about 10 cm;
8 flowing into said reactor over said wafer kept at a temperature between
9 about 25°C and about 400°C, a precursor gas of a cyclic siloxane at a flow rate between

10 about 5 sccm and about 1000 sccm, and a second precursor gas of organic molecules at a
11 flow rate between about 5 sccm and about 1000 sccm, while keeping a pressure in said
12 reactor between about 50 mTorr and about 5000 mTorr;
13 depositing an ultralow-k film on said wafer under a RF power density
14 between about 0.05 W/cm^2 and about 2.0 W/cm^2 ; and
15 annealing said ultralow-k film at a temperature not less than about 300°C
16 for at least about 0.25 hour.

1 34. A method for fabricating a thermally stable ultralow-k film comprising
2 the steps of:
3 providing a parallel plate type plasma enhanced chemical vapor deposition
4 (PECVD) reactor;
5 positioning a wafer on a substrate chuck having an area between about 500
6 cm^2 and about 600 cm^2 , and maintaining a gap between the wafer and a top electrode
7 between about 1 cm and about 7 cm;
8 flowing a precursor gas of a cyclic siloxane into said reactor over said
9 wafer kept at a temperature between about 60°C and about 200°C at a flow rate between
10 about 25 sccm and about 200 sccm and a second precursor of organic molecules at a flow
11 rate between about 10 sccm and about 120 sccm while keeping a pressure in said reactor
12 between about 100 mTorr and about 3000 mTorr;
13 depositing an ultralow-k film on said wafer under a RF power density
14 between about 0.25 W/cm^2 and about 0.8 W/cm^2 ; and
15 annealing said ultralow-k film at a temperature not less than about 300°C
16 for at least about 0.25 hour.

1 35. An electronic structure having layers of insulating material as
2 intralevel or interlevel dielectrics in a wiring structure comprising:
3 a pre-processed semiconducting substrate having a first region of metal
4 embedded in a first layer of insulating material;
5 a first region of conductor embedded in a second layer of insulating
6 material formed of an ultralow-k material, said ultralow-k material comprising Si, C, O

1 and H, and a multiplicity of nanometer-sized pores, said ultralow-k material having a
2 dielectric constant of not more than about 2.8, said second layer of insulating material
3 being in intimate contact with said first layer of insulating material, said first region of
4 conductor being in electrical communication with said first region of metal; and
5 a second region of conductor being in electrical communication with said
6 first region of conductor and being embedded in a third layer of insulating material
7 comprising said ultralow-k material, said third layer of insulating material being in
8 intimate contact with said second layer of insulating material.

1 36. The electronic structure according to Claim 35, further comprising a
2 dielectric cap layer situated between said second layer of insulating material and said
3 third layer of insulating material.

1 37. The electronic structure according to Claim 35, further comprising:
2 a first dielectric cap layer between said second layer of insulating material
3 and said third layer of insulating material; and
4 a second dielectric cap layer on top of said third layer of insulating
5 material.

1 38. The electronic structure according to Claim 36, wherein said dielectric
2 cap layer is formed of a material selected from the group consisting of silicon oxide,
3 silicon nitride, silicon oxynitride, refractory metal silicon nitride, silicon carbide, silicon
4 carbo-oxide, and carbon doped oxides and their hydrogen-containing compounds.

1 39. The electronic structure according to Claim 38, wherein said refractory
2 metal silicon nitride includes a refractory metal selected from the group consisting of Ta,
3 Zr, Hf and W.

1 40. The electronic structure according to claim 37, wherein said first
2 dielectric cap layer and said second dielectric cap layer are formed of a material selected
3 from the group consisting of silicon oxide, silicon nitride, silicon oxynitride, refractory

1 metal silicon nitride, silicon carbide, silicon carbo-oxide, carbon doped oxides and their
2 hydrogen-containing compounds.

1 41. The electronic structure according to Claim 40, wherein said refractory
2 metal silicon nitride includes a refractory metal selected from the group consisting of Ta,
3 Zr, Hf and W.

1 42. The electronic structure according to Claim 35, wherein said first layer
2 of insulating material is one selected from the group consisting of silicon oxide, silicon
3 nitride, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), and other doped
4 varieties of these materials.

1 43. The electronic structure according to Claim 35, further comprising:
2 a diffusion barrier layer of a dielectric material deposited on at least one of
3 said second layer of insulating material and said third layer of insulating material.

1 44. The electronic structure according to Claim 35, further comprising:
2 a dielectric reactive ion etching (RIE) hard mask/polish stop layer on top
3 of said second layer of insulating material, and
4 a dielectric diffusion barrier layer on top of said RIE hard mask/polish
5 stop layer.

1 45. The electronic structure according to Claim 35, further comprising:
2 a first dielectric RIE hard mask/polish stop layer on top of said second
3 layer of insulating material;
4 a first dielectric diffusion barrier layer on top of said first dielectric RIE
5 hard mask/polish stop layer;
6 a second dielectric RIE hard mask/polish stop layer on top of said third
7 layer of insulating material; and

1 a second dielectric diffusion barrier layer on top of said second dielectric
2 RIE hard mask/polish stop layer.

1 46. The electronic structure according to claim 45, further comprising:
2 a dielectric cap layer between an interlevel dielectric of an ultralow-k
3 material and an intralevel dielectric of an ultralow-k material.

1 47. An electronic structure having layers of insulating material as
2 intralevel or interlevel dielectrics in a wiring structure comprising:
3 a pre-processed semiconducting substrate having a first region of metal
4 embedded in a first layer of insulating material; and
5 at least one first region of conductor embedded in at least one second layer
6 of insulating material formed of an ultralow-k material, said ultralow-k material
7 consisting essentially of Si, C, O and H, and a multiplicity of nanometer-sized pores, said
8 ultralow-k material having a dielectric constant of not more than about 2.8, one of said at
9 least one second layer of insulating material being in intimate contact with said first layer
10 of insulating material, one of said at least one first region of conductor being in electrical
11 communication with said first region of metal.

1 48. The electronic structure according to Claim 47, further comprising:
2 a dielectric cap layer situated between each said at least one second layer
3 of insulating material.

1 49. The electronic structure according to Claim 47, further comprising:
2 a first dielectric cap layer between each of said at least one second layer of
3 insulating material; and
4 a second dielectric cap layer on top of said topmost second layer of
5 insulating material.

1 50. The electronic structure according to Claim 49, wherein said first
2 dielectric cap layer and said second dielectric cap layer are formed of an ultralow-k
3 material.

1 51. The electronic structure according to Claim 49, wherein said first
2 dielectric cap layer and said second dielectric cap layer are formed of a modified
3 ultralow-k material.

1 52. The electronic structure according to Claim 48, wherein said dielectric
2 cap layer is formed of a material selected from the group consisting of silicon oxide,
3 silicon nitride, silicon oxynitride, refractory metal silicon nitride, silicon carbide, silicon
4 carbo-oxide, carbon doped oxides and their hydrogen-containing compounds.

1 53. The electronic structure according to Claim 52, wherein said refractory
2 metal silicon nitride includes a refractory metal selected from the group consisting of Ta,
3 Zr, Hf and W.

1 54. An electronic structure having layers of insulating material as
2 intralevel or interlevel dielectrics in a wiring structure comprising:
3 a pre-processed semiconducting substrate having a first region of metal
4 embedded in a first layer of insulating material;
5 a first region of conductor embedded in a second layer of insulating
6 material; said second layer of insulating material being in intimate contact with said first
7 layer of insulating material, said first region of conductor being in electrical
8 communication with said first region of metal;
9 a second region of conductor being in electrical communication with said
10 first region of conductor and being embedded in a third layer of insulating material, said
11 third layer of insulating material being in intimate contact with said second layer of
12 insulating material;
13 a first dielectric cap layer between said second layer of insulating material
14 and said third layer of insulating material, and

15 a second dielectric cap layer on top of said third layer of insulating
16 material wherein said first and said second dielectric cap layers are formed of an
17 ultralow-k dielectric material, said ultralow-k material comprising Si, C, O and H, and a
18 multiplicity of nanometer-sized pores, said ultralow-k material having a dielectric
19 constant of not more than about 2.8.

1 55. An electronic structure having layers of insulating material as
2 intralevel or interlevel dielectrics in a wiring structure comprising:
3 a pre-processed semiconducting substrate having a first region of metal
4 embedded in a first layer of insulating material;
5 a first region of conductor embedded in a second layer of insulating
6 material, said second layer of insulating material being in intimate contact with said first
7 layer of insulating material, said first region of conductor being in electrical
8 communication with said first region of metal;
9 a second region of conductor being in electrical communication with said
10 first region of conductor and being embedded in a third layer of insulating material, said
11 third layer of insulating material being in intimate contact with said second layer of
12 insulating material; and
13 a diffusion barrier layer formed of a material comprising an ultralow-k
14 dielectric material deposited on at least one of said second layer and said third layer of
15 insulating material, said ultralow-k material comprising Si, C, O and H, and a multiplicity
16 of nanometer-sized pores, said ultralow-k material having a dielectric constant of not
17 more than about 2.8.

1 56. An electronic structure having layers of insulating material as
2 intralevel or interlevel dielectrics in a wiring structure comprising:
3 a pre-processed semiconducting substrate having a first region of metal
4 embedded in a first layer of insulating material;
5 a first region of conductor embedded in a second layer of insulating
6 material, said second layer of insulating material being in intimate contact with said first

1 layer of insulating material, said first region of conductor being in electrical
2 communication with said first region of metal;
3 a second region of conductor being in electrical communication with said
4 first region of conductor and being embedded in a third layer of insulating material, said
5 third layer of insulating material being in intimate contact with said second layer of
6 insulating material;
7 a reactive ion etching (RIE) hard mask/polish stop layer on top of said
8 second layer of insulating material, and
9 a diffusion barrier layer on top of said RIE hard mask/polish stop layer,
10 wherein said RIE hard mask/polish stop layer and said diffusion barrier layer are formed
11 of a an ultralow-k dielectric material, said ultralow-k material comprising Si, C, O and H,
12 and a multiplicity of nanometer-sized pores, said ultralow-k material having a dielectric
13 constant of not more than about 2.8.

1 57. An electronic structure having layers of insulating material as
2 intralevel or interlevel dielectrics in a wiring structure comprising:
3 a pre-processed semiconducting substrate having a first region of metal
4 embedded in a first layer of insulating material,
5 a first region of conductor embedded in a second layer of insulating
6 material, said second layer of insulating material being in intimate contact with said first
7 layer of insulating material, said first region of conductor being in electrical
8 communication with said first region of metal;
9 a second region of conductor being in electrical communication with said
10 first region of conductor and being embedded in a third layer of insulating material, said
11 third layer of insulating material being in intimate contact with said second layer of
12 insulating material;
13 a first RIE hard mask/polish stop layer on top of said second layer of
14 insulating material;
15 a first diffusion barrier layer on top of said first RIE hard mask/polish stop
16 layer;

17 a second RIE hard mask/polish stop layer on top of said third layer of
18 insulating material; and
19 a second diffusion barrier layer on top of said second RIE hard
20 mask/polish stop layer, wherein said RIE hard mask/polish stop layers and said diffusion
21 barrier layers are formed of a ultralow-k dielectric material comprising Si, C, O and H,
22 and a multiplicity of nanometer-sized pores, said ultralow-k material having a dielectric
23 constant of not more than about 2.8.

1 58. The electronic structure according to Claim 57, further comprising a
2 dielectric cap layer formed of a material comprising said ultralow-k dielectric material
3 situated between an interlevel dielectric layer and an intralevel dielectric layer.

1 59. A method for fabricating a thermally stable ultralow dielectric constant
2 film comprising the steps of:
3 providing a plasma enhanced chemical vapor deposition (PECVD) reactor;
4 positioning a substrate in said PECVD reactor;
5 flowing a first precursor gas comprising cyclic siloxane molecules into
6 said PECVD reactor;
7 flowing at least a second precursor gas comprising organic molecules with
8 ring structures having C, H and O atoms into said PECVD reactor; and
9 depositing a film comprising Si, C, O and H and a multiplicity of
10 nanometer-sized pores on said substrate in presence of CO₂ or CO₂ and O₂.

1 60. The method according to Claim 59, further comprising a step of
2 mixing said first precursor gas with CO₂.

1 61. The method according to Claim 59, further comprising a step of
2 mixing said first precursor gas and said second precursor gas with CO₂ or a mixture of
3 CO₂ and O₂.

1 62. The method according to Claim 59, wherein said PECVD reactor is of
2 a parallel plate type reactor.

1 63. The method according to Claim 59, wherein said film is optionally
2 heated after deposition at a temperature not less than about 300°C for at least about 0.25
3 hours.

1 64. The method according to Claim 59, wherein said film has a dielectric
2 constant of not more than about 2.8.

1 65. The method according to Claim 59, wherein said film has a dielectric
2 constant of not more than about 2.3.

1 66. The method according to Claim 59, wherein said film has a dielectric
2 constant in a range from about 1.5 to about 2.5.

1 67. The method according to Claim 59, wherein said film comprises:
2 between about 5 and about 40 atomic percent of Si;
3 between about 5 and about 45 atomic percent of C;
4 between 0 and about 50 atomic percent of O; and
5 between about 10 and about 55 atomic percent of H.

1 68. The method according to Claim 59, further comprising the step of:
2 providing a parallel plate reactor having an area of a substrate chuck
3 between about 300 cm² and about 700 cm², and a gap between the substrate and a top
4 electrode between about 1 cm and about 10 cm.

1 69. The method for fabricating a thermally stable ultralow dielectric
2 constant film according to Claim 62, said method further comprising the step of:
3 applying a RF power to an electrode of said parallel plate PECVD reactor.

1 70. The method according to Claim 59, further comprising a step of:
2 heat treating said film at a temperature not higher than about 300°C for a
3 first time period and heat treating said film at a temperature not lower than about 300°C
4 for a second time period, said second time period being longer than said first time period.

1 71. The method according to Claim 69, wherein said second time period is
2 at least about ten times that of said first time period.

1 72. The method according to Claim 59, wherein said cyclic siloxane is
2 selected from the group consisting of: tetramethylcyclotetrasiloxane and
3 octamethylcyclotetrasiloxane.

1 73. The method according to Claim 59, wherein said cyclic siloxane is
2 tetramethylcyclotetrasiloxane.

1 74. The method according to Claim 59, wherein said organic molecules
2 comprise species of fused rings including ring structures that impart significant ring
3 strain, wherein said ring structures that impart significant ring strain include rings of 3, 4,
4 7 or more atoms.

1 75. The method according to Claim 59, wherein said organic molecules
2 are cyclopentene oxide.

1 76. The method according to Claim 59, wherein said step of depositing the
2 film further comprises the steps of:
3 setting a temperature for said substrate at between about 25°C and about
4 400°C; and
5 setting a RF power density at between about 0.05 W/cm² and about 2.0
6 W/cm².

1 77. The method according to Claim 60, wherein said step of depositing the
2 film further comprises:
3 setting a flow rate for said cyclic siloxane at between about 5 sccm and
4 about 1000 sccm and setting a flow rate for said CO₂ at between about 25 sccm and 1000
5 sccm.

1 78. The method according to Claim 77, wherein said flow rate for said
2 cyclic siloxane is set at between about 25 sccm and about 200 sccm and said flow rate
3 for said CO₂ is set at between about 50 sccm and about 500 sccm.

1 79. The method according to Claim 60, wherein said step of depositing
2 said film further comprises:
3 setting flow rates said for said organic molecules at between about 5 sccm
4 and about 1000 sccm.

1 80. The method Claim 79, wherein said flow rates for said organic
2 molecules are at between about 25 sccm and about 200 sccm.

1 81. The method according to Claim 61, wherein said step of depositing the
2 film further comprises:
3 setting a flow rate for said CO₂ at between about 25 sccm and about 1000
4 sccm and setting a flow rate for said O₂ at between about 0.5 sccm and about 50 sccm.

1 82. The method according to Claim 81, wherein said flow rate for said
2 CO₂ is set at between about 50 sccm and about 500 sccm and said flow rate for said O₂ is
3 set at between about 1 sccm and about 30 sccm.

1 83. The method according to Claim 59, wherein said step of depositing
2 said film further comprises:

1 setting a pressure for said PECVD reactor at between about 50 mTorr and
2 about 5000 mTorr.

1 84. The method according to Claim 83, wherein said pressure for said
2 PECVD reactor is between about 100 mTorr and about 4000 mTorr.

1 85. The method according to Claim 59, wherein said step of depositing
2 said film further comprises:
3 setting a flow rate ratio of organic molecules of cyclopentene oxide to
4 cyclic siloxane of tetramethylcyclotetrasiloxane to between about 0.1 and about 0.7.

1 86. The method for fabricating a thermally stable ultralow dielectric
2 constant film according to Claim 83, wherein said flow rate ratio of said cyclopentene
3 oxide to said tetramethylcyclotetrasiloxane is between about 0.2 and about 0.4.

1 87. The method according to Claim 59, said method further comprising:
2 providing a parallel plate plasma enhanced chemical vapor deposition
3 chamber.

1 88. The method according to Claim 59, wherein plasma in said PECVD
2 reactor is run in a continuous mode.

1 89. The method according to Claim 59, wherein plasma in said PECVD
2 reactor is run in a pulsed mode.

1 90. The method according to Claim 68, wherein a change in the area of
2 said substrate chuck by a factor, X, changes the RF power by a factor, X.

1 91. The method according to Claim 68, wherein a change in the area of the
2 substrate chuck by a factor, Y, and a change in the gap between a gas distribution plate

1 and the substrate chuck by a factor, Z, changes gas flow rates by a factor, YZ, such that
2 residence time in plasma is maintained.

1 92. The method according to claim 77, wherein when said PECVD reactor
2 includes a plurality of depositions stations then the flow rates of said cyclic siloxane are
3 multiplied by a total number of deposition stations in said PECVD reactor.

1 93. A method for fabricating a thermally stable ultralow-k film comprising
2 the steps of:
3 providing parallel plate type plasma enhanced chemical vapor deposition
4 (PECVD) reactor;
5 positioning a pre-processed wafer on a substrate chuck having an area
6 between about 300 cm² and about 700 cm² and maintaining a gap between said wafer and
7 a top electrode between about 1 cm and about 10 cm;
8 flowing a first precursor gas comprising cyclic siloxane molecules into
9 said PECVD reactor;
10 flowing at least a second precursor gas comprising organic molecules with
11 ring structures having C, H and O atoms; and
12 depositing an ultralow-k film on said wafer in presence of CO₂ or CO₂ and
13 O₂.

1 94. The method according to Claim 93, further comprising a step of
2 mixing said first precursor gas with CO₂.

1 95. The method according to Claim 93, further comprising a step of
2 mixing said first precursor gas and at least said second precursor gas with CO₂ or a
3 mixture of CO₂ and O₂.

1 96. The method according to Claim 94, wherein said step of depositing the
2 film further comprises:

1 setting a flow rate for said first precursor at between about 5 sccm and
2 about 1000 sccm and setting a flow rate for said CO₂ at between 25 sccm and 1000 sccm.

1 97. The method according to Claim 96, wherein said flow rate for said
2 first precursor is set at between about 25 sccm and about 200 sccm and said flow rate for
3 said CO₂ is set at between about 50 sccm and about 500 sccm.

1 98. The method according to Claim 95, wherein the step of depositing the
2 film further comprises:
3 setting a flow rate for said CO₂ at between about 25 sccm and about 1000
4 sccm and a flow rate for O₂ at between about 0.5 sccm and about 50 sccm.

1 99. The method according to Claim 98, wherein said flow rate for said
2 CO₂ is set at between about 50 sccm and about 500 sccm and said flow rate for said O₂ is
3 set at between about 1 sccm and about 30 sccm.

1 100. A method for fabricating a thermally stable ultralow-k film
2 comprising the steps of:
3 providing a parallel plate type plasma enhanced chemical vapor deposition
4 (PECVD) reactor;
5 positioning a wafer on a substrate chuck having an area between about 300
6 cm² and about 700 cm², and maintaining a gap between the wafer and a top electrode
7 between about 1 cm and about 10 cm;
8 flowing into said reactor over said wafer kept at a temperature between
9 about 25°C and about 400°C, a first precursor gas of a cyclic siloxane, and a second
10 precursor gas of organic molecules, while keeping a pressure in said reactor between
11 about 50 mTorr and about 5000 mTorr;
12 depositing an ultralow-k film on said wafer under a RF power density
13 between about 0.05 W/cm² and about 2.0 W/cm² in presence of CO₂ or CO₂ and O₂; and
14 annealing said ultralow-k film at a temperature not less than about 300°C
15 for at least about 0.25 hour.

1 101. The method according to Claim 100, further comprising a step of
2 mixing said first precursor gas with CO₂.

1 102. The method according to Claim 100, further comprising a step of
2 mixing said first precursor gas and at least said second precursor gas with CO₂ or a
3 mixture of CO₂ and O₂.

1 103. The method according to Claim 101, wherein said step of depositing
2 the film further comprises:
3 setting a flow rate for said first precursor at between about 5 sccm and
4 about 1000 sccm and setting a flow rate for said CO₂ at between about 25 sccm and about
5 1000 sccm.

1 104. The method according to Claim 103, wherein said flow rate for said
2 first precursor is set at between about 25 sccm and about 200 sccm and said flow rate for
3 said CO₂ is set at between about 50 sccm and about 500 sccm.

1 105. The method according to Claim 102, wherein the step of depositing
2 the film further comprises:
3 setting a flow rate for said CO₂ at between about 25 sccm and about 1000
4 sccm and a flow rate for O₂ at between about 0.5 XX sccm and about 50 YY sccm.

1 106. The method according to Claim 105, wherein said flow rate for said
2 CO₂ is set at between about 50 sccm and about 500 sccm and said flow rate for said O₂ is
3 set at between about 1 sccm and about 30 sccm.

1 107. A method for fabricating a thermally stable ultralow-k film
2 comprising the steps of:
3 providing a parallel plate type plasma enhanced chemical vapor deposition
4 (PECVD) reactor;

1 positioning a wafer on a substrate chuck having an area between about 500
2 cm^2 and about 600 cm^2 , and maintaining a gap between the wafer and a top electrode
3 between about 1 cm and about 7 cm;
4 flowing a first precursor gas of a cyclic siloxane into said reactor over said
5 wafer kept at a temperature between about 60°C and about 200°C and a second precursor
6 of organic molecules while keeping a pressure in said reactor between about 100 mTorr
7 and about 3000 mTorr;
8 depositing an ultralow-k film on said wafer under a RF power density
9 between about 0.25 W/cm^2 and about 0.8 W/cm^2 in presence of CO_2 or CO_2 and O_2 ; and
10 annealing said ultralow-k film at a temperature not less than about 300°C
11 for at least about 0.25 hour

1 108. The method according to Claim 107, further comprising a step of
2 mixing said first precursor gas with CO_2 .

1 109. The method according to Claim 107, further comprising a step of
2 mixing said first precursor gas and at least said second precursor gas with CO_2 or a
3 mixture of CO_2 and O_2 .

1 110. The method according to Claim 108, wherein said step of depositing
2 the film further comprises:
3 setting a flow rate for said first precursor at between about 5 sccm and
4 about 1000 sccm and setting a flow rate for said CO_2 at between about 25 XX sccm and
5 about 1000 sccm.

1 111. The method according to Claim 110, wherein said flow rate for said
2 first precursor is set at between about 25 sccm and about 200 sccm and said flow rate for
3 said CO_2 is set at between about 50 sccm and about 500 sccm.

1 112. The method according to Claim 109, wherein the step of depositing
2 the film further comprises:

1 setting a flow rate for said CO₂ at between about 25 sccm and about 100
2 sccm and a flow rate for O₂ at between about 0.5XX sccm and about 50 sccm.

1 113. The method according to Claim 112, wherein said flow rate for said
2 CO₂ is set at between about 50 sccm and about 500 sccm and said flow rate for said O₂ is
3 set at between about 1 sccm and about 30 sccm.

1 114. A method for fabricating a thermally stable ultralow dielectric
2 constant film comprising the steps of:
3 providing a plasma enhanced chemical vapor deposition (PECVD) reactor;
4 positioning a substrate in said PECVD reactor;
5 flowing a first precursor gas comprising cyclic siloxane molecules using
6 CO₂ as a carrier gas into said PECVD reactor;
7 flowing at least a second precursor gas comprising organic molecules with
8 ring structures having C, H and O atoms into said PECVD reactor; and
9 depositing a film comprising Si, C, O and H and a multiplicity of
10 nanometer-sized pores on said substrate in presence of said CO₂.

1 115. The method according to Claim 114, wherein a flow rate of said first
2 precursor is from about 5 sccm and about 1000 sccm and a flow rate of said CO₂ is from
3 about 25 sccm and about 1000 sccm.

1 116. The method according to Claim 115, wherein the flow rate for said
2 first precursor is from about 25 sccm to about 200 sccm and the flow rate of said CO₂ is
3 from about 50 sccm to about 500 sccm.

1 117. A method for fabricating a thermally stable ultralow dielectric
2 constant film comprising the steps of:
3 providing a plasma enhanced chemical vapor deposition (PECVD) reactor;
4 positioning a substrate in said PECVD reactor;

1 flowing a first precursor gas comprising cyclic siloxane molecules into
2 said PECVD reactor;
3 flowing at least a second precursor gas comprising organic molecules with
4 ring structures having C, H and O atoms into said PECVD reactor;
5 flowing CO₂ into said PECVD reactor;
6 depositing a film comprising Si, C, O and H and a multiplicity of
7 nanometer-sized pores on said substrate in presence of said CO₂.

1 118. The method according to Claim 117, wherein a flow rate of said CO₂
2 is from about 25 sccm and about 1000 sccm.

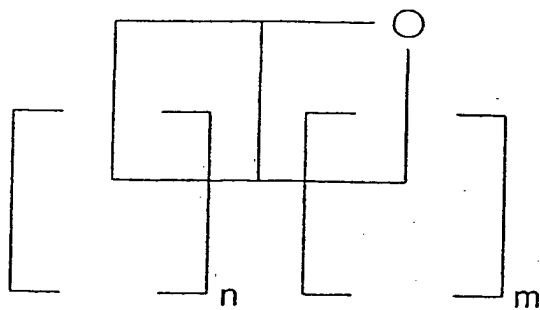
1 119. The method according to Claim 118, wherein the flow rate of said
2 CO₂ is from about 50 sccm to about 500 sccm.

1 120. A method for fabricating a thermally stable ultralow dielectric
2 constant film comprising the steps of:
3 providing a plasma enhanced chemical vapor deposition (PECVD) reactor;
4 positioning a substrate in said PECVD reactor;
5 flowing a first precursor gas comprising cyclic siloxane molecules into
6 said PECVD reactor;
7 flowing at least a second precursor gas comprising organic molecules with
8 ring structures having C, H and O atoms into said PECVD reactor;
9 flowing a mixture of CO₂ and O₂ into the PECVD reactor; and
10 depositing a film comprising Si, C, O and H and a multiplicity of
11 nanometer-sized pores on said substrate in presence of said CO₂ and O₂.

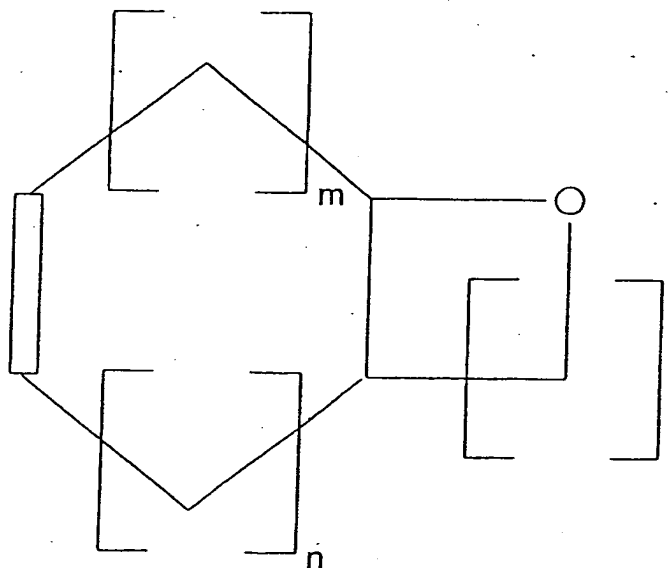
1 121. The method according to Claim 120, wherein the CO₂ is flown at a
2 flow rate from about 25 sccm to about 1000 sccm and said O₂ is flown at a flow rate from
3 about 0.5 sccm to about 50 sccm.

- 1 122. The method according to Claim 121, wherein the flow rate of CO₂ is
- 2 form about 50 sccm to about 500 sccm and the flow rate of said O₂ is from about 1 sccm
- 3 to about 30 sccm.

1/6



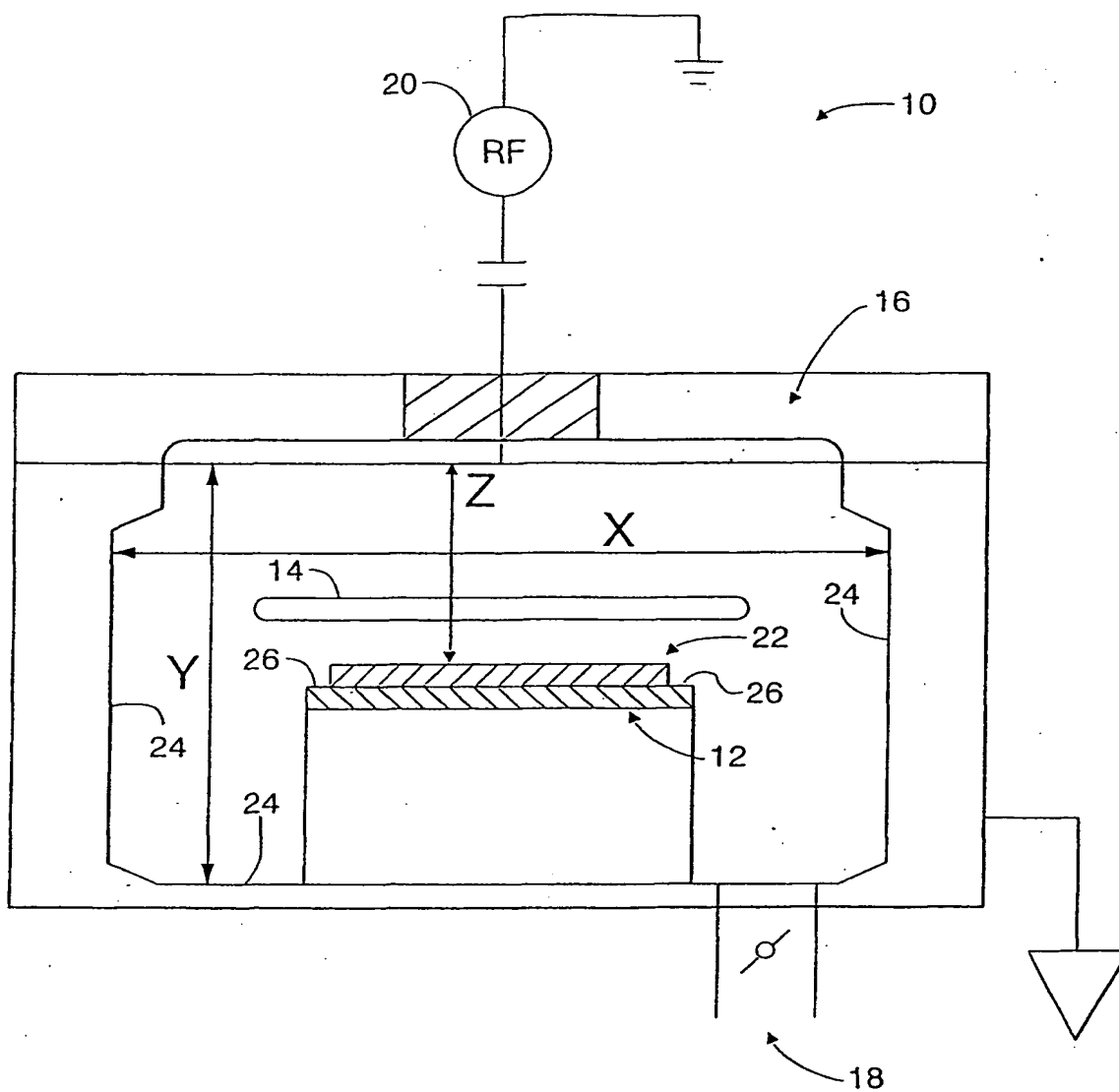
where $m = 0$ to 5 and $n = 0$ to 10

FIG. 1

where $l = 0$ to 5 , $m = 0$ to 10 ; and $n = 0$ to 10

FIG. 2

2/6

**FIG. 3**

3/6

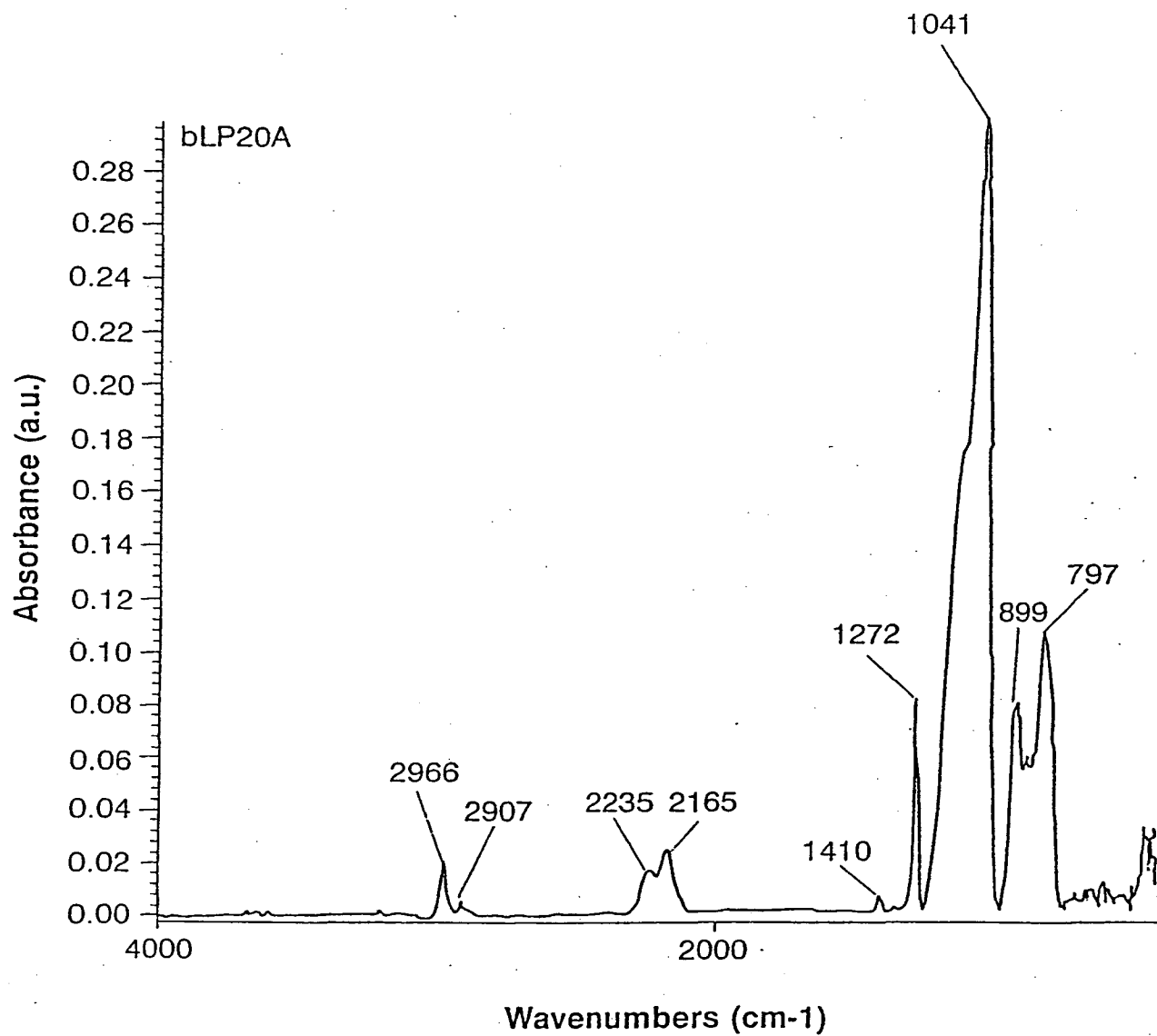
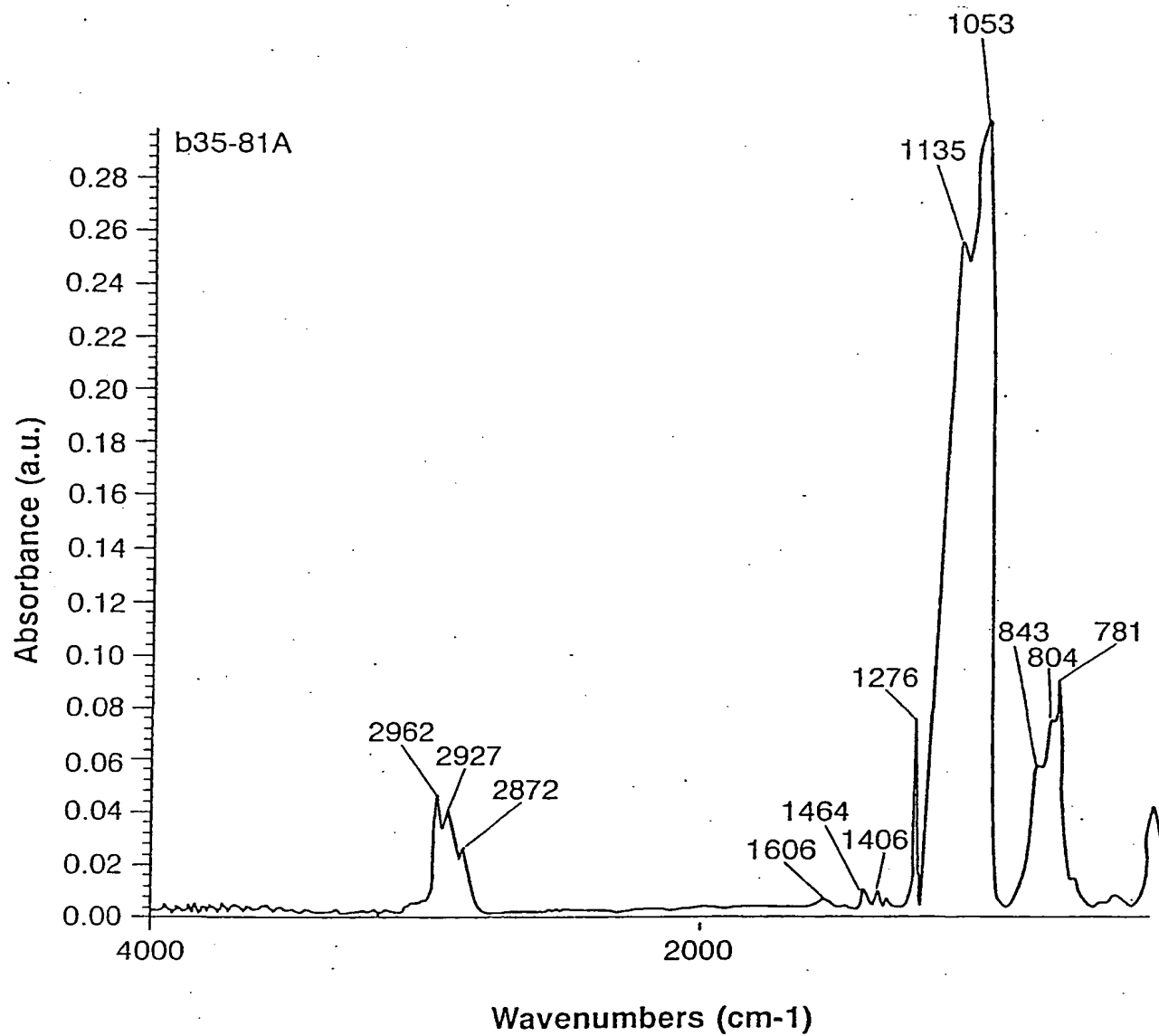


FIG. 4

4/6

**FIG. 5**

5/6

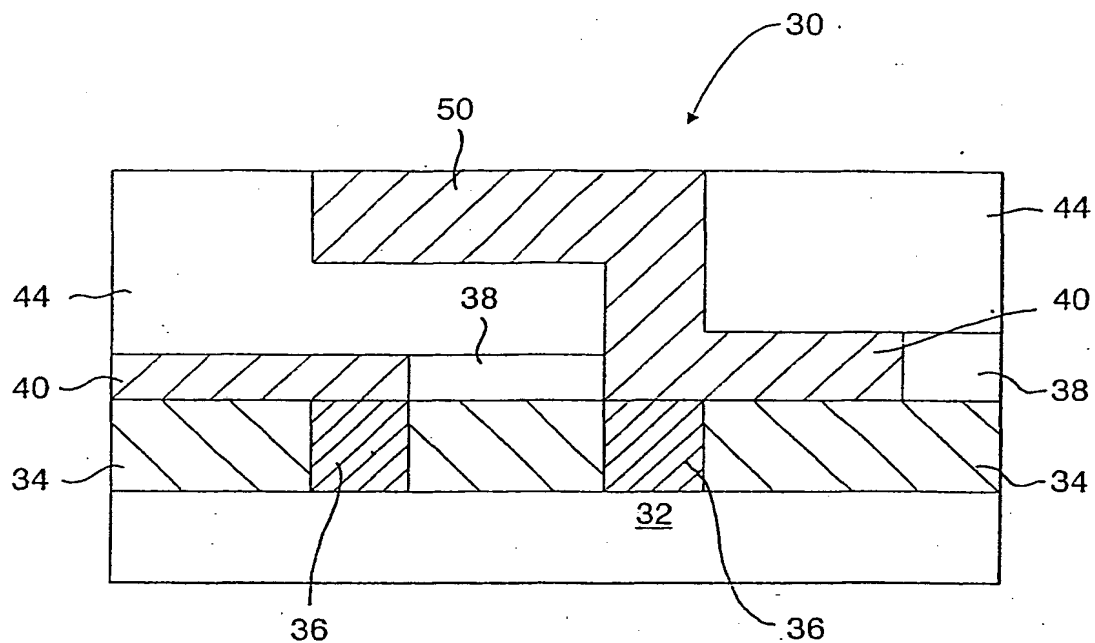


FIG. 6

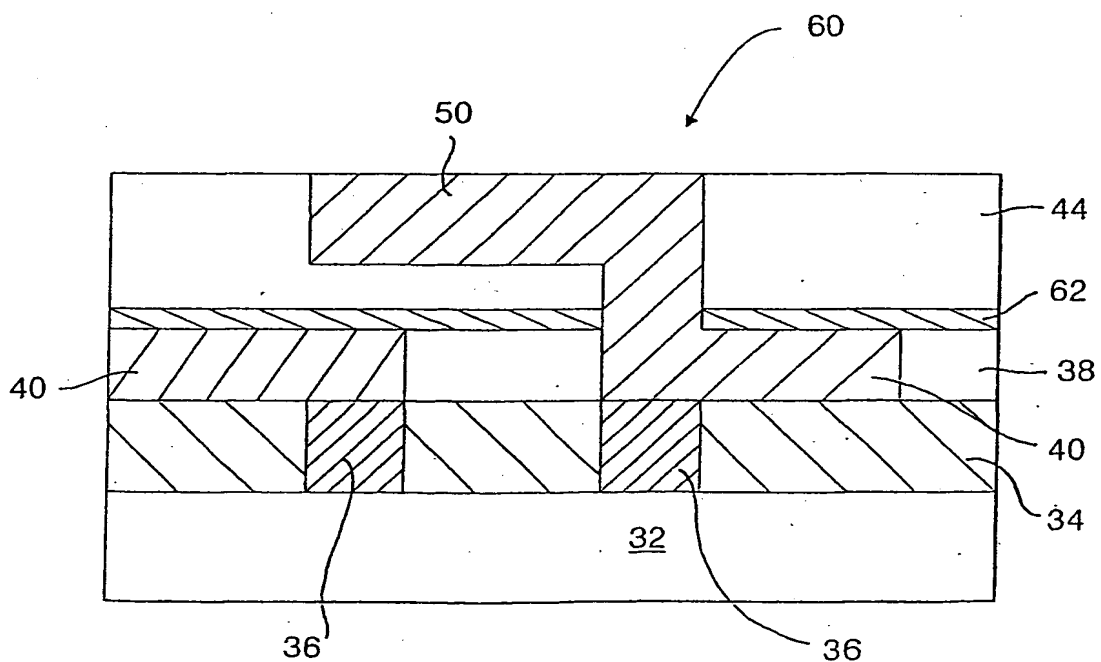


FIG. 7

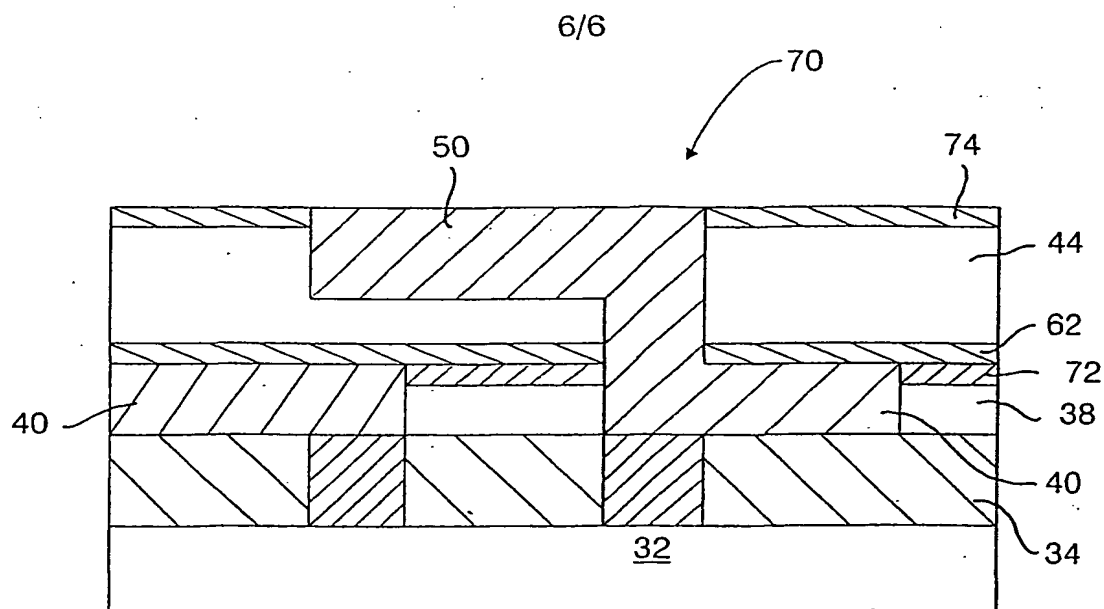


FIG. 8

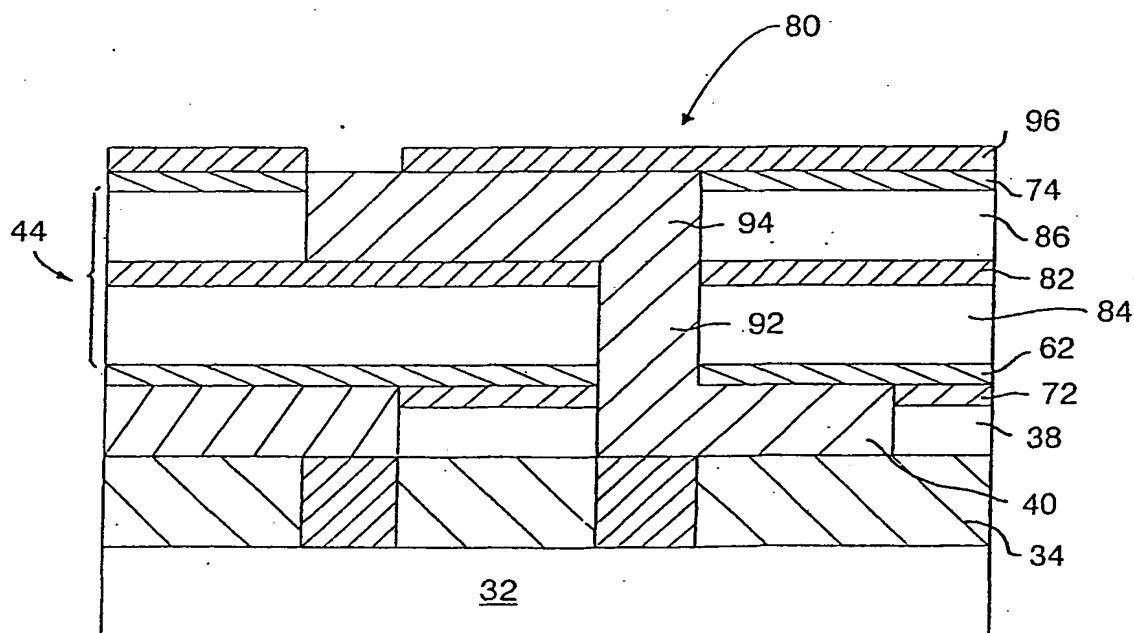


FIG. 9

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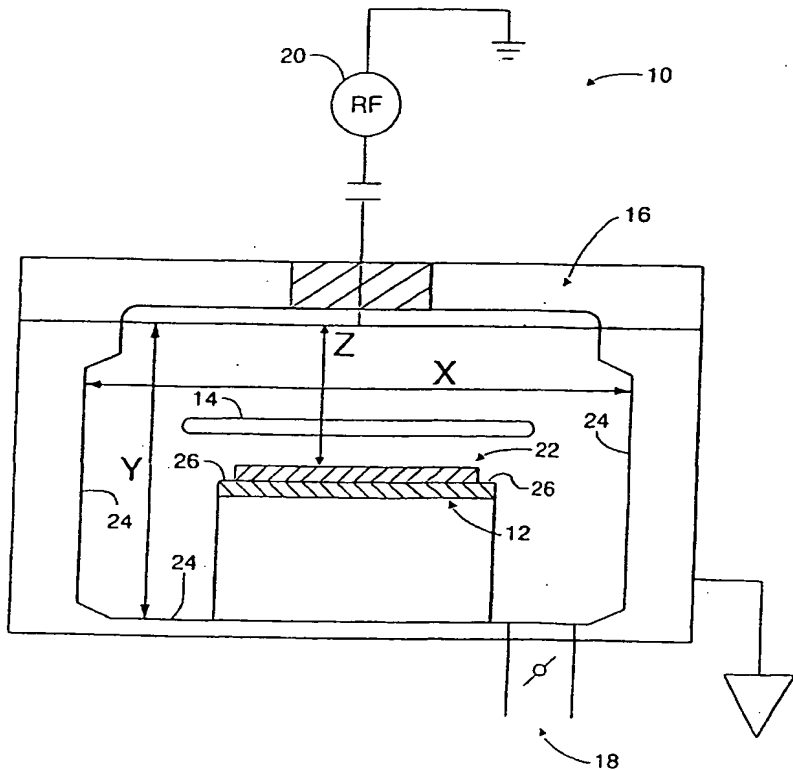
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: AN ULTRALOW DIELECTRIC CONSTANT MATERIAL AS AN INTRALEVEL OR INTERLEVEL DIELECTRIC IN A SEMICONDUCTOR DEVICE, A METHOD FOR FABRICATING THE SAME, AND AN ELECTRONIC DEVICE CONTAINING THE SAME



(57) Abstract: A method for fabricating a thermally stable ultralow dielectric constant film comprising Si, C, O and H atoms in a parallel plate chemical vapor deposition process utilizing plasma enhanced chemical vapor deposition ("PECVD") process is disclosed. Electronic devices containing insulating layers of thermally stable ultralow dielectric constant materials that are prepared by the method are further disclosed. To enable the fabrication of thermally stable ultralow dielectric constant film, specific precursor materials are used, such as, cyclic siloxanes and organic molecules containing ring structures, for instance, tetramethylcyclotetrasiloxane and cyclopentene oxide. To stabilize plasma in the PECVD reactor and thereby improve uniformity of the deposited film, CO₂ is added to TMCTS as a carrier gas, or CO₂ or a mixture of CO₂ and O₂ are added to the PECVD reactor.

WO 02/043119 A3

INTERNATIONAL SEARCH REPORT

International Application No

PC 7 S 01/50830

A. CLASSIFICATION OF SUBJECT MATTER

PC 7 C23C16/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 00 24050 A (APPLIED MATERIALS INC) 27 April 2000 (2000-04-27) the whole document	1,2,5-8, 13,14, 27-31
Y	EP 0 826 791 A (MATSUSHITA ELECTRIC IND CO LTD) 4 March 1998 (1998-03-04) page 20, line 11 -page 21, line 35	1,2,5-8, 13,14, 27-31
Y	US 6 068 884 A (LOPATA EUGENE ET AL) 30 May 2000 (2000-05-30) column 5, line 49 - line 53 column 6, line 49 - line 67 -/--	1,2,5-8, 13,14, 27-31

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

18 September 2002

Date of mailing of the international search report

18.12.02

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PC JS 01/50830

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>GRILL A ET AL: "Low dielectric constant SiCOH films as potential candidates for interconnect dielectrics" LOW-DIELECTRIC CONSTANT MATERIALS V. PROCEEDINGS (MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS VOL:565), LOW-DIELECTRIC CONSTANT MATERIALS V. SYMPOSIUM, SAN FRANCISCO, CA, USA, 5-8 APRIL 1999, pages 107-116, XP001099051 1999, Warrendale, PA, USA, Mater. Res. Soc, USA ISBN: 1-55899-472-6 the whole document -----</p>	27,28

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 01/50830

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1, 2, 5-8, 13, 14, 27-31

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1, 2, 5-8, 13, 14, 27-31

A PECVD method for fabricating a thermally stable ultralow dielectric constant film comprising the steps of:

- using a first precursor gas comprising cyclic siloxane;
- using a second precursor gas comprising organic molecules with ring structures having C, H and O atoms; and depositing a film comprising Si, C, O and H and nanometer-sized pores,
- wherein the first precursor gas is mixed with an inert carrier gas.

The features of claims 5-8, 13, 14, 27-31 are considered trivial or have been found during the search for the first invention.

2. Claims: 32 and 3, 9, 10, 26 (in combination with claim 1)

A PECVD method for fabricating a thermally stable ultralow dielectric constant film comprising the steps of:

- using a first precursor gas comprising cyclic siloxane molecules;
- using a second precursor gas comprising organic molecules with ring structures having C, H and O atoms into said PECVD reactor; and
- depositing a film on said substrate, wherein the PECVD reactor is a parallel plate reactor with a particular chuck area and a particular gap is maintained between wafer and top electrode.

3. Claims: 33, 34 and 4, 17-23 (in combination with claim 1)

A PECVD method for fabricating a thermally stable ultralow dielectric constant film comprising the steps of:

- using a first precursor gas comprising cyclic siloxane molecules;
- using a second precursor gas comprising organic molecules with ring structures having C, H and O atoms into said PECVD reactor; and
- depositing a film on said substrate, wherein the PECVD reactor is a parallel plate reactor with a particular chuck area and a particular gap is maintained between wafer and top electrode, and wherein temperature, gas flow rates, pressure and power density are defined, and wherein the film is annealed.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

4. Claims: 59-92, 114-116, 117-119, 120-122

A PECVD method for fabricating a thermally stable ultralow dielectric constant film comprising the steps of:

- using a first precursor gas comprising cyclic siloxane;
- using a second precursor gas comprising organic molecules with ring structures having C, H and O atoms; and
- depositing a film comprising Si, C, O and H and nanometer-sized pores,

- wherein CO₂ is flowed into the reactor chamber.

In case of claims 59-92 the film is deposited in the presence of CO₂ or CO₂ and O₂.

In case of claims 114-116 the CO₂ is used as a carrier gas.

In case of claims 120-122 O₂ is additionally flowed into the reactor chamber.

5. Claims: 93-99

A PECVD method for fabricating a thermally stable ultralow dielectric constant film comprising the steps of:

- using a first precursor gas comprising cyclic siloxane molecules;
 - using a second precursor gas comprising organic molecules with ring structures having C, H and O atoms into said PECVD reactor; and
 - depositing a film on said substrate,
- wherein the PECVD reactor is a parallel plate reactor with a particular chuck area and a particular gap is maintained between wafer and top electrode, and wherein the film is deposited in the presence of CO₂ or CO₂ and O₂.

6. Claims: 100-106, 107-113

A PECVD method for fabricating a thermally stable ultralow dielectric constant film comprising the steps of:

- using a first precursor gas comprising cyclic siloxane molecules;
 - using a second precursor gas comprising organic molecules; and
 - depositing a film on said substrate,
- wherein the PECVD reactor is a parallel plate reactor with a particular chuck area and a particular gap is maintained between wafer and top electrode, and wherein temperature, pressure and power density are defined, and wherein the film is annealed, and wherein the film is deposited in the presence of CO₂ or CO₂ and O₂.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

7. Claims: 11, 12 (in combination with claim 1)

Additionally a particular annealing sequence is used.

8. Claims: 15, 16, 24, 25 (in combination with claim 1)

The organic molecules of the second precursor comprise fused rings with rings of 3, 4, 7 or more atoms.

9. Claims: 35-46, 47-53, 54, 55, 56, 57-58

One or more insulating layer formed of ultralow-k material comprising Si, C, O and H and nanopores;
wherein metal is embedded in the layers (claims 35-46, 47-53) or
wherein the layer is a "cap layer" (claim 54) or
wherein the layer is a "diffusion barrier layer" (claim 55)
or
wherein the layers are "hard mask layers" and "diffusion barrier layers" (claims 56, 57-58).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC 01/50830

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